RHEOLOGY OF PEROXIDE MODIFIED RECYCLED HIGH DENSITY POLYETHYLENE

A thesis submitted in fulfilment of the requirements for the degree of Master of Engineering

By Harisinh Parmar
B.Eng. (Chemical)

School of Civil, Environmental and Chemical Engineering
Science, Engineering and Technology Portfolio
RMIT University
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DECLARATION

I, Harisinh Parmar, certify that except where due acknowledgment has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried in the School of Civil, Environmental and Chemical Engineering, RMIT University, Melbourne, Australia during the period of July 2005 to December, 2007.

Harisinh Parmar

December 5, 2007.

DEDICATION

I dedicate this thesis to

Shri Mandavraiji (Suryanarayana Bhagvan),

my loving Parents

and

family members.

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ABSTRACT

Consumption of plastics has increased exponentially, in line with the world's population. Not surprisingly this is reflected in enormous growth of the plastic industry especially during the last five decades. Commensurate with this, waste produced from plastics consumption has created a major environmental problem. Many types of waste disposal methods have been used all over the world so far, but all of them have disadvantages. Furthermore, some methods are responsible for the generation of green house gases and further contribution to global warming. Recently, reduction of green house gas emission has become a target of most industries. Plastic recycling and reuse breaks the cycle of endless production of virgin polymer and thus contributes to a net reduction of green house gas emission.

Recycling of plastics should produce materials with improved properties to replace virgin plastics for a variety of applications. Improvement in the properties of recycled plastics can be achieved by blending with other plastics, by filler addition and by modification using free radical initiators. Introduction of the free radical initiator (organic peroxide) during reprocessing of the recycled plastics has been found to offer significant property improvements to the recycled materials. Extremely small amounts of a free radical initiator (typically ranging between 0.01 wt% to 0.2 wt%) is capable of enhancing the properties of the recycled plastics to a great extent.

This project investigates the use of free radical initiators in the recycling of post consumer recycled high density polyethylene using reactive extrusion. Both molecular and rheological characterisation of recycled and reprocessed materials was carried out and this was followed by tensile testing of the modified materials to satisfy end use applications such as packaging and drainage piping.

Post consumer recycled high density polyethylene (R-HDPE) resin and virgin high density polyethylene (V-HDPE) were reactively extruded with low concentrations of dicumyl peroxide (DCP) and 1, 3 1, 4 Bis (tert- butylperoxyisopropyl) Benzene (OP2) respectively in a twin screw extruder in order to produce modified materials with varying composition (0.0 wt%, 0.02 wt%, 0.05 wt%, 0.07 wt%, 0.10 wt% and 0.15 wt%) of both organic peroxides. Morphological characterisation using modulated

differential scanning calorimetry (MDSC) demonstrated that there is a decrease in the crystallinity level for all the modified samples.

Shear rheological tests were carried out to study the structure of the modified materials within the linear viscoelastic region. Viscoelastic parameters, such as storage modulus (G'), loss modulus (G") and complex viscosity (η*) showed improvement at all frequencies tested with increase in both peroxides compositions. Higher improvements were experienced with OP2 modified V-HDPE and R-HDPE. R-HDPE showed greatest improvement in viscoelastic properties due to the inclusion of low level of carbon black as stabilizer. However, increase in peroxide loading causes appearance of the divergence of complex viscosity profile from Newtonian plateau to non-Newtonian slope analogous to finite yield stress region. Formation of long chain branches or extended chain mechanism causes disappearance of terminal zone and shear thinning like characteristics.

Extensional rheological study, using the melt strength tester, was carried out to evaluate the response of the modified material to extensional deformation. However, melt strength is not a well-defined rheological property because of non-uniform strain and temperature along a drawn filament. Melt strength of V-HDPE and R-HDPE was enhanced with peroxide modifications. Alignment of the long chain branched molecules in the uni-directional stretching requires more force to stretch the polymer strand leading to enhancement in the melt strength. On the other hand, these long chain branched molecules restrict motion of the chain due to the higher relaxation time, thus can not resist rupture of the strand at higher draw ratio. Thus, extensibility was found to decrease with increased melt strength. Instabilities like draw resonance and ductile fracture were experienced with peroxide loading leading to processing limitations. Extensional viscosity was found to increase with all modified samples. This enhancement was also experienced with recycled modified materials.

Molecular characterisation was done to assess the molecular level changes during reactive extrusion and peroxide modification process for all the modified materials. Gel Permeation Chromatography (GPC) of all the peroxide modified materials showed increase in weight average (M_w) and number average (M_n) molecular weight with respect to the peroxide loading. In addition, increments in M_w than M_n indicated increased branch length. Branching index (g') also showed lower values as branching

mechanisms developed. Environmental stress cracking resistance was also measured to evaluate the suitability of the modified material in terms of the targeted pipe application. Resistance to stress crack growth increased with peroxide modifications for both virgin and R-HDPE. However, elongation properties were found to decrease with peroxide loading.

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NOMENCLATURE

A	Cross section Area, m^2
F	Draw Force (Rheotens Experiment), N
g’	Branching Index, Dimensionless
G’	Storage Modulus, Pa
G”	Loss Modulus, Pa
G*	Complex Modulus, Pa
H	Height between two plates in ARES, cm
L	Length, m
Ls	Draw Distance (Rheotens Experiment), cm
Mn	Number-Average molecular Weight, g/mol
Mw	Average Molecular Weight, g/mol
Q	Volumetric flow Rate (Rheotens Experiment), kg/s
R	Radius of the plate, cm
t	Time, s
T	Torque, N-m
Tm	Melting temperature, °C
Tg	Glass transition temperature, °C
Tc	Crystallisation temperature, °C
V	Draw Ratio, Dimensionless
υ	Velocity at Nip rollers, mm/s
υ_0	Velocity at Die Exit, mm/s

Greek Symbols

ε	Extensional Strain, Dimensionless
$\dot{\varepsilon}$	Extensional Strain Rate, Dimensionless
$\dot{\gamma}_R$	Shear Rate, s^{-1}
γ	Sinusoidal Strain, Dimensionless
γ_0	Sinusoidal Strain Amplitude, Dimensionless
δ	Phase Angle, Degree
η^*	Complex Viscosity, Pa.s
$\eta(\gamma)$	Steady Shear Viscosity, Pa.s
η^+_E	Transient Extensional Viscosity, Pa.s
η_E	Extensional Viscosity, Pa.s
λ	Relaxation Time, s
ω	Angular Frequency, rad/s
γ_c	Critical Value of Strain, Dimensionless
Ω	Constant angular velocity oscillation, rad/s
$[\eta]$	Intrinsic Viscosity, dl/g

CHAPTER 1. INTRODUCTION

1.1. INTRODUCTION

Recycled plastics have gained significant interest in both the fundamental and applied research areas due to the environmental and social impact. It is imperative that society has to lead by example to 'reuse' and 'recycle' of plastics. In addition to savings in cost, the modified recycled plastics provide added advantages. Their improved physical, mechanical, chemical and electrical properties such as light weight, high tensile strength, elasticity, stiffness, toughness, resistance to corrosive environment and compete well with the virgin plastics. The accumulation of plastic waste in landfill together with the increasing market share of plastic blow moulded and injection moulded products has encouraged industries around the world to consider recycling post consumer high density polyethylene (R-HDPE) for variety of purposes.

R-HDPE exhibits poor melt processability. It also lacks melt strength, which is important for uniform wall thickness and resist puncture failure of blow moulded products. Melt strength properties of R-HDPE can be improved by using additives during blending or compounding prior to or during extrusion. Introduction of long chain branching network of entanglements in linear polyolefins results in extraordinary increase in melt strength.

1.2. PROBLEM STATEMENT

Plastics are unavoidable part of entire society. Unique properties of plastics make it attractive to designers, manufactures and packagers. However, modifications of properties pose challenges of frequent testing of material properties, standardization of material properties and frequent product testing. As recycling of plastics becomes inevitable for sustainable development, it is facing same challenges as virgin plastics as mentioned above. In fact, the challenges become more significant in recycled plastics as their properties are usually not as good as their virgin counterparts. It is known that plastics loose some properties after its first use, but it is difficult to know which properties will be lost.

Particularly in the case of post consumer recycled HDPE, elongation at break is affected to a greater extent by the content of recycled HDPE (Pattanakul et al., 1991). Degradation and contamination also affect the properties to some extent. Overall, however, the recycled HDPE from milk bottles was found to have useful properties almost similar to that of virgin resin. Thus it can be used for different applications when combined with virgin HDPE at appropriate concentration, for different applications.

One of the potential applications of post consumer recycled HDPE resin is in non pressure pipes manufacturing. Principal applications of these pipes include gas distribution, water-service lines, slurry transport, sewage and fire mains and power ducting. High pressure pipe applications require resistance to slow crack growth but low or non-pressure pipe applications are generally subject to significantly lower permanent stress levels. Currently post consumer recycled HDPE resin is used to make corrugated drainage pipe. Approximately 90% or more of recycled HDPE is used in combination with virgin material to optimize overall material properties. In Australia, corrugated pipe manufacturing sector represents only 5% of the total market. Rural pipe application has good market potential than corrugated pipes.

Recycled milk bottle resin would not be suitable for piping application without modification, particularly in its resistance to stress cracking. This milk bottle resin can also be used in manufacturing of blow moulded products such as detergent and shampoo bottles. Milk bottle resin needs to have higher bubble stability to form bubble of uniform thickness. Bubble stability in the blow moulding and film blowing process can be controlled by elongational viscosity, melt strength and degree of long chain branching (Field et al., 1999).

The following are the important challenges related to post consumer HDPE resin recycling and its application.

1. Post consumer recycled HDPE resin has inferior properties such as low elongation at break, and is prone to stress crack growth and simultaneous degradation and crosslinking during reprocessing. These inferior properties narrow downs its application windows.

2. Lack of industry support and awareness of recycled products.

3. Recycled HDPE can not be used for direct food contact approval.

4. It is very necessary to understand the properties-reprocessing relationship which can be very useful to develop material with improved properties and hence broadening the application window.

Extensive literature illustrates that, not enough work has been done on stress cracking resistance and melt strength of recycled HDPE. It has been observed that, free radical initiator such as organic peroxide is capable of improvement in the recycled material properties even with very low concentrations. Moreover, peroxide modification process results in improvements in properties than observed in blending techniques. Therefore, different organic peroxides were used to introduce lower degree of long chain branching in the post consumer recycled HDPE. Peroxide modified recycled materials were tested in terms of its melt strength and environmental stress cracking resistance (ESCR) to check its suitability in piping applications. Molecular, rheological and thermal performance of modified recycled materials is studied as a part of this research work in order to understand modification process at molecular level.

1.3. AIMS AND OBJECTIVES OF THE RESEARCH PROJECT

Post consumer recycled HDPE resin has potential application in packaging and drainage pipe industry. In addition, reactive extrusion of recycled HDPE with organic peroxide might be very significant in terms of enhancement of melt strength and stress cracking resistance as well as other rheological properties of the modified recycled HDPE. This project aims to understand the role of two different organic peroxides separately in reactive extrusion process and how the final material properties would be affected.

The objectives of this research are to:

- Examine and evaluate existing approaches that has been used to improve properties of R-HDPE or other polyolefins.
- Select two different organic peroxides based on their chemical properties, half lives and typical crosslinking temperature.

- Produce organic peroxide treated virgin high density polyethylene (V-HDPE) and R-HDPE resin with varying concentration of organic peroxide by reactive extrusion process with a laboratory-scale twin- screw extruder.
- Carry out thermal characterisation by modulated differential scanning calorimetry (MDSC). This characterisation process is essential as it shows crystallinity and melting behaviour of the modified material.
- Conduct shear rheological studies of the organic peroxide treated V-HDPE and R-HDPE resins. It is important to examine the deformation and flow of the modified material under the influence of applied stress.
- Investigate extensional rheological properties of the prepared organic peroxide modified V-HDPE and R-HDPE. This characterisation gives the real picture of simultaneous shear and extensional deformation during polymer processing.
- Carry out molecular characterisation by gel permeation chromatography (GPC). It is a vital characterisation as it reveals molecular weight and its distribution of the modified material.
- Develop relation between shear and extensional rheology with the molecular characterisation of modified materials.
- Characterise modified material in terms of resistance towards stress cracking particularly for rural pipe application.
- Carry out tensile and impact testing headed for modified materials behaviour to stress and strain properties.

1.4. OUTLINE OF THIS THESIS

Chapter 2: This chapter presents a literature survey on current post consumer HDPE recycling approaches, reactive extrusion process, introduction of organic peroxide as crosslinking agent followed by effects of reactive extrusion of post consumer recycled HDPE and organic peroxide on final material properties.

Chapter 3: This chapter presents detail information about all the materials, equipments used and experimental procedures. Detailed descriptions of all materials required in this study are given in the first part. Second part is a combination of all the equipments and experimental methods used for material and sample preparation followed by further analysis.

Chapter 4: In this chapter results and discussion are presented. Materials are analysed to evaluate the changes in the properties. In the first and second part, these materials are reviewed in terms of their shear rheological and uniaxial extensional deformation response. Results are presented and discussed in terms of viscoelastic and melt strength properties. All modified materials are evaluated with intention to verify thermal behaviour in the following part. Results are presented and analysed as a function of crystallinity, melting point and heat of fusion change due to peroxide modification. In the third part, gel permeation chromatography (GPC) results evaluating the molecular weight averages, molecular weight distribution, and long chain branching in the modified V-HDPE and R-HDPE are presented. Detailed discussion is given to verify long chain branching structure on the basis of GPC results presented. Finally, modified V-HDPE and R-HDPE samples are characterised in terms of their response to tensile stress and strain. Results for environmental stress cracking resistant are also presented and discussed.

Chapter 5: Conclusions derived from results and recommendations are presented in this chapter.

CHAPTER 2. LITERATURE REVIEW

2.1. IMPORTANCE OF PLASTICS AND ITS RECYCLING

Plastics and chemical products are building blocks of the modern economy. Plastics and chemicals industry is Australia's fourth largest manufacturing sector. It provides essential raw materials to many other sectors, including automotive, healthcare and pharmaceuticals, education and information technology, packaging, construction and consumer appliances. Their product and process innovations make a substantial and continuing contribution to the quality of life enjoyed by all Australians.

Polyethylene, such as high density and linear low density polyethylene have many advantages over other packaging materials available in the market such as light weight, high melt strength and ease of processing. It is not expensive; used extensively and cause minor environmental implications. Its strength and lightweight-ness nature acquired first place in the category of packaging materials for many applications. Russell and Oneill (1993) have shown that the use of plastics as a packaging material can help to reduce weight, volume and packaging cost. These benefits are more enhanced by effective management of plastic waste.

Plastic recycling from post consumer waste stream has been shown to produce the following benefits:

- Conservation of non-renewable fuels and energy
- Reduced solid waste
- Reduced emissions of CO_2 and nitrogen oxide

In Australia, 1,480,154 tonnes of plastics consumed in the year of 2005 and 109,407 tonnes of them consumed alone in Victoria and the recycling rate is only half of its total consumption (PACIA, 2006). Rest of plastics ended up with landfill or other means of disposal which are dangerous to the environment. Moreover, 36.16 MJ/kg energy required to produce virgin material while 4.39 MJ/Kg of energy is required for recycling the equivalent amount of material counterparts. All of these facts and figures have only one unified conclusion that plastics are very important but their effective

management after usage and its recycling is more important. Life cycle of recycled plastics can be increased and the use of non-renewable sources of the nature can be reduced.

2.2. HIGH DENSITY POLYETHYLENE RECYCLING

(a) **(b)**

Figure 2-1 (a) General formula of PE (b) a molecule of linear PE or HDPE

Polyethylene (PE) polymerized under low temperature and pressure results in linear structure with only a few, short branches. This type of PE is called high-density polyethylene (HDPE)(figure 2-1)(Strong, 2006). As the name implies polymer chains in HDPE can easily pack tightly and form crystalline structures, thus increasing density (0.96 g/cc). Because of its excellent moisture barrier properties and chemical resistance, it has found various applications and considered as ubiquitous material. However, HDPE, like all types of polyethylene, is limited to those food packaging applications that do not require an oxygen or CO_2 barrier. In film form, HDPE is used in snack food packaging and cereal box liners; in blow-moulded bottle form, for milk and non-carbonated beverage bottles; and in injection-moulded tub form, for packaging margarine, whipped toppings and deli foods. Because HDPE has good chemical resistance, it is used for packaging many household as well as industrial chemicals such as detergents, bleach and acids. General uses of HDPE include injection-moulded beverage cases, bread trays as well as films for grocery sacks and bottles for beverages and household chemicals.

Polyethylene is not biodegradable and will persist in the environment for hundred of years for example, polyethylene film containers last for 80-200 years while bottles can last more than that. Light weight and moisture resistant make PE non degradable even in the water. Polyethylene waste is also disturbing marine life. Incineration method of this waste disposal produces green house gases. Hence, recycling is the best unique solution to overcome these problems.

Recycled HDPE can be used for wide range of applications. A major potential application for recycled HDPE resin (coloured and dairy) in flood and drainage pipe production. However, due to the concern about the low ESCR of recycled HDPE, producers tend to use low grade virgin HDPE. Improvements in ESCR of recycled HDPE will open huge market for recycled materials.

2.2.1. Barriers to HDPE recycling

Although, HDPE recycling is very important for both economical and environmental reasons, it has two major barriers.

1. Contaminations and
2. Poor suitability for high quality applications

2.2.1.1. Contamination

Coloured HDPE from the collection process is susceptible to wide variations in quality and consistency. These factors undermine the theoretically superior performance, improved processability and wider application of this material. Contamination from container residue, different colours of these collected bottles and other plastics are the main reason for the low quality and hence low price and low recycling rates for this material. Contamination level of just few parts per millions (ppm) can diminish finished product performance. Moreover, caps and temper evidence ring can cause colour tinting of the resin, which may also undesirable.

2.2.1.2. Poor suitability for high quality application

Poor suitability of the post consumer HDPE dairy grade resin for the high performance applications is major barrier to increase recycling rate. HDPE dairy grade resin is relatively cheap and well suited for thin-walled monolayer blow moulding applications like refrigerated fresh milk and juice bottles. Without any addition or modification, dairy grade or coloured HDPE recyclate have generally been limited to heavy walled injection or intrusion moulding application and extrusion. Typically, products made from recycled HDPE are relatively inferior in value and physical performance. Poor environmental stress cracking resistance (ESCR) of recycled HDPE limits its use in manufacturing of only heavy walled products which do not need high ESCR, impact strength and toughness.

2.3. CURRENT APPROACHES TO IMPROVE RECYCLED HDPE PROPERTIES

There are mainly two ways to improve properties of post consumer recycled HDPE resin.

Blending of R-HDPE with/without compatibilizers

Blending techniques enable to provide mixed polymer properties. Blending is exercised in the industrial practice. The main reason to blend recycled polymer with virgin or recycled polymer is to obtain a material with better processability and improved properties. Miscible blends found to achieve improved properties. However, immiscible blend makes miscible with the help of compatibilizers. Blending of post consumer recycled HDPE with other polyolefins can be divided into two parts based on different blending approaches.

1. Blends of two polymers.
2. Blends of several polymers.

2.3.1. Blends of two polymers

Recycled HDPE is ideal for blow-moulding applications, but it is less appropriate for use in the injection moulding and some extrusion applications. Blending with polyolefins is one of the approaches to improve properties of recycled HDPE for wide range of applications. Significant efforts have been made since 1980s in the development and research of virgin, (Cho et al., 1998a, Schuman et al., 1998, Zhang et al., 1999, Rana, 1998, Schellenberg and Fienhold, 1998, Hu et al., 1987, Gupta et al., 1992a, Gupta et al., 1992b, Gupta et al., 1993, Garcia-Rejon and Alvarez, 1987) and recycled (Viksne and Bledzki, 1998, Rueda et al., 1994, Rueda et al., 1996, Albano et al., 1998b, Suarez et al., 1999) HDPE/LDPE and HDPE/LLDPE blends. Miscibility in the melt was reported (Cho et al., 1998b, Schuman et al., 1998) for the HDPE/LLDPE system and co-crystallization of the components in the solid state was reported (Gupta et al., 1992a, Rana, 1998, Gupta et al., 1992b, Hu et al., 1987, Gupta et al., 1993, Nadkarni and Jog, 1991) for the same. In connection with LLDPE blends, miscibility and/or co-crystallization of HDPE and LLDPE results in the improvement of its mechanical properties (Cho et al., 1998b, Gupta et al., 1992b, Gupta et al., 1993).

LLDPE is used with HDPE to improve mechanical properties of the overall blend but recycled HDPE/LLDPE blends showed poor mechanical properties due to greater difference in melt flow index (MFI) and/or molecular weight between blend components (Kukaleva et al., 2003b). On the other hand, this blend is not used for injection moulding applications because they do not have high shear thinning viscosity behaviour. However, milk bottle grade HDPE modified by less viscous LLDPE improve the rheological behaviour of the entire blend.

Some researchers (Zhang et al., 1999, Stafford, 1965, Robertson and Paul, 1973, Rueda et al., 1996, Miller et al., 2001a) reported co-crystallization of LDPE and HDPE segments. Hence, it is very difficult to state about miscibility of this system. However, miscibility of the system can be controlled by degree of branching and concentration of the component (Hill et al., 1991, Garcia-Rejon and Alvarez, 1987, Alamo et al., 1994, Wignall et al., 1995, Alamo et al., 1997, Agamalian et al., 1999). In addition, Miller et al (2001b) reported for LDPE/R-HDPE blend that melting point and crystallinity peaks were observed up to 50 vol% of HDPE. One melting peak was observed beyond this composition of R-HDPE, indicating miscibility of the LDPE/R-HDPE blend.

For HDPE/LDPE blends, high shear thinning behaviour of this blend expected to use in injection moulding applications. Moreover, improved mechanical properties of the R-HDPE/LDPE blend were reported (Kukaleva et al., 2003b). Partial miscibility in the melt state and co-crystallization ability in the solid state results in this improved properties. However, co-crystallization of linear and branched types of polyethylenes is a rare phenomenon. Kukaleva et al (2003b) concluded that, R-HDPE/LDPE blend is more compatible than V-HDPE/ R-HDPE blend due to less regular molecular structure and higher polydispersity index of LDPE. Formation of branched structure and tie chain molecules resulting from oxidation and chain scission process within R-HDPE backbone might be the possible reason for lower compatibility of V-HDPE/R-HDPE blend. Miller et al (2001a) did extensive work on thermal, rheological and mechanical properties of R- HDPE blends with virgin HDPE, LDPE and LLDPE respectively. Miller et al (2001a) found that the modulus ratio (which is defined as the modulus of the blend divided by modulus of virgin material) decreased with LDPE compositions. Elongation at break was increased up to 40% compositions of recycled HDPE. Quick decline in the elongation at break was observed on or beyond 50% composition of R-HDPE (Teh, 1983). Morphological analysis of LDPE/R-HDPE blends show

compatibility or a partial miscibility that improves the mechanical properties with an increase in the concentration of R-HDPE. However, there was not any change observed in the lamellar thickness of the polymer beyond 50% composition of recycled HDPE and this factor has adverse effect on tensile properties.

Recycled HDPE from milk bottles are often being contaminated by polypropylene homo-polymer and co-polymer from the milk bottle caps (Kukaleva et al., 2003a). In order to use these recycled HDPE for injection moulding process, it is blended with polypropylene polymers in order to reduce viscosity and enhance ease of processing without much compromising in mechanical properties. They found that, both homopolymer and copolymer polypropylene has very high value of modulus and yield strength. Both polypropylenes were investigated for the purpose of viscosity reduction. Moreover, the homopolymer is more useful at very high and low shear rates while the copolymer is the more efficient in the mid range of shear rates ($10^2 – 10^3$ sec^{-1}). Albano et al (1998b) also worked on recycled HDPE/PP blends and synergism in the Young's modulus below 50 wt % of R-HDPE. Morphological outcomes of the same blends support the mechanical results as small size of the semi-crystalline region (spherulites) observed in it. The value of elongation at break depicts the incompatibility of the blends and no significant change in crystallinity observed.

2.3.2. Blend of several polymers and their compatibilization

Blending of several polymers was employed to achieve good balance between desired properties. Kukaleva et al (2003a) reported improvement in mechanical properties of ternary blend of recycled HDPE with LDPE and PP (77%/10%/13% wt/wt respectively). However, reduction in viscosity (25%-30%) was observed only at low shear rates/frequencies. Albano et al (1998a) made an attempt to make blend of several polymers. They mixed recycled LDPE and HDPE and then third polymer was virgin PP or LDPE. 12% of recycled blend is the optimal concentrations in terms of mechanical properties like elongation at break and impact strength improvement. It is possible to use 20% recycled blend with PP and 10% with LDPE.

High density polyethylene (HDPE) and polyethylene terephthalate (PET) have been extensively used mainly in packaging applications and comprise large amount of plastics waste. Pracella et al (2004) had tried to make blends of HDPE/PET as an alternative solution of these large amounts of post-consumer waste. They found that,

binary blends of R-PET with HDPE or other recycled polyethylene show the typical morphological features of incompatible systems with a poor dispersion of the components and no interfacial adhesion between matrix and dispersed phase. The compatibility of immiscible blends can be improved by reactive and non-reactive compatibilization. Baker et al (2001) achieved the reduction of interfacial tension and improvement of interfacial adhesion by compatibilization of immiscible blends. Dagli and Kamdar (1994) discussed the effect of component addition on the reactive compatibilization of HDPE/PET blends. Ethylene glycidyl methacrylate copolymer (EGMA) was used and they tried different modes of component addition and finally concluded that the best practice is to first blend EGMA with HDPE and then PET was blended with EGMA/HDPE blend. Finally, they got improved mechanical and morphological properties. Moreover, Pawlak et al (2002) reported that the elongation at break and impact strength of reactively blended recycled HDPE/PET blends increased with the addition of ethylene-glycidyl methacrylate copolymer (EGMA) or maleic anhydride grafted styrene-ethylene butylene-styrene (SEBS-g-MA). These mechanical properties related to the phase distribution. Reactive blending results in the increase in viscosities of the compatibilized blends.

Extensive works have been done on post consumer PET/ HDPE compatibilization (Pracella et al., 2002, Laurienzo et al., 2001, Dimitrova et al., 2000). The improvement of the mechanical and morphological properties of the blends can be achieved by adding maleic anhydride grafted polyethylene (PE-g-MA) as a compatibilizer (Jarukumjorn and Chareunkvun, 2006). Jarukumjorn and Chareunkvun (2006) further observed that, as compatibilizer loading bought mechanical properties improvement and dispersed phase size decreased due to enhanced interaction between matrix and dispersed phase in morphological analysis. Viscosity of the blend was linearly proportional to HDPE composition in the blend. Overall blend viscosity increased due to the interaction between the compatibilizer and polymers. It was reported that the decrease in crystallinity proves compatibility of these blends.

Recycled HDPE/PS blends exhibit solid dispersion type of morphology with poor mechanical properties. $CaCO_3$ was introduced to improve mechanical properties of this blend, particularly stiffness and impact strength (Sahnoune et al., 2003). In addition, R-HDPE/PS/$CaCO_3$ blend has high stiffness but lower impact strength. Elastomercopolymer (SEBS-g-MA) was introduced in order to compensate for the

embrittlement caused by $CaCO_3$ filler. Final blend exhibit both improved stiffness and impact strength. Use of fillers/clay in the recycled HDPE instead of other polyolefins or other polymers, in order to improve overall material properties, was recently developed by some researchers (Atikler et al., 2006, Lei et al., 2007). Improvements in mechanical properties were observed by both the researchers with addition of clay/ fillers. In addition, fly ash is more effective in terms of interfacial adhesion between fly ash filler and HDPE matrix, hence improved mechanical properties (Atikler et al., 2006).

2.3.3. Chemical modification of polymer by organic peroxide

In recent years, chemical modification of post consumer recycled material was done in order to achieve improved properties for first grade applications. The use of free radical initiator is an inexpensive and rapid way of obtaining target properties in polyolefins. Moreover, small concentration of initiator leads to synergetic improvement of polyolefins properties. This method involves reaction of a polymer with a vinyl containing monomers, or a mixture of monomers capable of forming joints or crosslinks onto the polymer backbone.

Polyolefins are cross-linked in three different way that is, by high radiation, thermochemical, and moisture cross-links. Among these, the thermochemical method is carried out by the addition of chemical, typically peroxide. The reaction is generally carried out in melt state and crosslinking occur at random locations (Venkatraman and Kleiner, 1989). This advantageous method is further gained with the use of batch mixture or screw extruders as chemical reactor, which allows the free-radical grafting reaction to occur without solvents (Hu et al., 2001).

Extensive study has been done by different researchers (Perez et al., 2002, Venkatraman and Kleiner, 1989, Kim and Kim, 1993a) towards chemical modifications of polyolefins. Perez et al (2002) reported improvement in molecular and rheological properties of four types of HDPE modified by organic peroxide. The vinyl group containing polymers demonstrated significant change in molecular weight for even low concentration of peroxide. Veankatraman and Kleiner (1989) worked on three (high radiation, thermochemical, and moisture crosslinking) different types of crosslinking and compared properties obtained from three different types. They reported lowest crystallinity with peroxide modification that proves high degree of branching. Kim and

Kim (1993b) also crosslinked high density polyethylene by reactive extrusion process using peroxide and two different co-agents which were used to avoid unwanted side reactions like chain scission and disproportionation. They also have studied the rheological, thermal and mechanical properties of the modified materials and found better enhancement in viscoelastic and thermal property with peroxide than with co-agents.

2.4. REACTIVE EXTRUSION OF POLYMERS

The use of extruders as continuous reactor, for processes such as polymerization, polymer modification or compatibilization of the polymer blends, involves technologies that are gaining popularity and compete well with conventional operations in terms of efficiency and economics. Reactive extrusion is an extruder-conducted process that involves a chemical reaction of the feed polymer. The feed polymer is modified by:

- changing its molecular weight
- grafting or adding a functional monomer to the polymer
- Reactive combination of one polymer with another.

Reactive extrusion provides the environment for melting, mixing and reaction of the polymer and additives. Adequate residence time at the proper temperature must be provided to carry out the reaction. The extruder conditions must be carefully controlled to allow the proper reaction. Twin-screw extruders are generally used in the reactive extrusion process. Polymer modification via reactive extrusion is intended to produce chemical changes that improve the properties of the material such as enhanced thermal stability, mechanical strength, elongation, adhesive strength and other mechanical properties. Schematic view of typical reactive extrusion process is shown in figure 2-2.

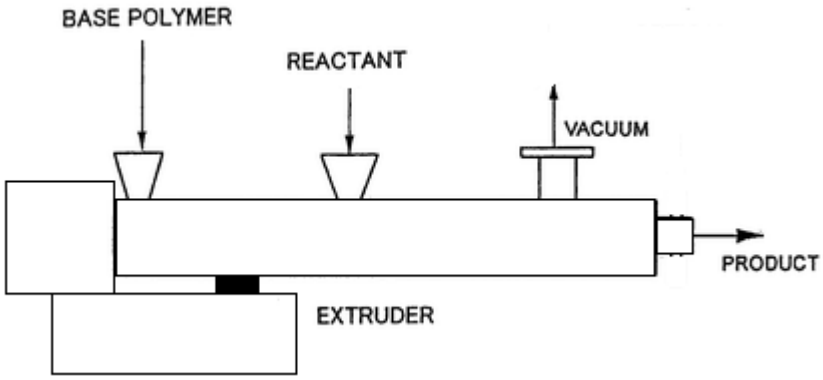


Figure 2-2 Diagram of typical reactive extrusion process

Many papers and reviews regarding different aspects of reactive extrusion have been summarized by Xanthos (1992). Types of chemical reactions performed by reactive extrusion have been classified as bulk polymerization, grafting reactions, interchain copolymer formation, coupling/cross-linking reactions, controlled-degradation and functionalization / functional group modification. Extensive work has been done on the reactive extrusion of polyolefins in the presence of different organic peroxides (Kim and Kim, 1993b, Suwanda and Balke, 1993b, Tang et al., 1989, Lachtermacher and Rudin, 1995a, Lachtermacher and Rudin, 1996b, Isac and George, 2001).

Recycled polyethylenes have also been modified using reactive extrusion where low or high peroxide concentrations were employed (Suwanda and Balke, 1993b, Suwanda and Balke, 1993a). Polyethylene undergoes crosslinking and end linking reactions to increase the degree of long chain branching, molecular weight and breadth of molecular weight distribution. At low peroxide concentrations, long chain branches are produced and hence the rheological properties are modified. At high peroxide concentrations, highly crosslinked materials are produced.

2.4.1. Types of reactive extrusion processes

There are many types of reactive extrusion processes. Reactive extrusion processes are divided based on type of reactions that take place in the extruder and the polymer and additive that are reacting. Following section covers two most widely used reactive extrusion processes

1. Controlled degradation of polymers
2. Grafting monomers onto polymers

2.4.1.1 Controlled degradation of polymers

Controlled degradation process of reactive extrusion involves breaking down of large chains of polymer in to smaller chains. The first commercialized process of reactive extrusion involved controlled degradation of polymer in the presence of free radical initiator like organic peroxide. Thermal degradation of peroxide leads to form active free radical and they react with the polymer chains and break it into small fractions. "Viscosity breaking" and "controlled rheology" processing is one of the typical process of reactive extrusion which involves polyolefins and copolymers of olefins. The chain length reduction of high molecular weight polypropylene is a typical controlled rheology process. Reaction between peroxide and polypropylene (PP) was carried out in the extruder; when PP was in the melt state. The temperature was controlled to decompose the peroxide. Peroxide addition is controlled to achieve desired molecular weight reduction. A narrower molecular weight distribution was also achieved. Experimental studies of this process using a single-screw extruder were conducted by Pabedinskas and Cluett (1994) and Tzoganakis et al (1988).

Pabedinskas and Cluett (1994) have presented the design and analysis of a process control for a reactive extrusion process of PP degradation. Continuous production of PP with desired properties (viscosity), regardless of variations in the feed material properties, was set as an objective. The viscosity of the PP was controlled by manipulating the feed concentration of the peroxide. The produced experimental model of the reactive degradation process describes the process dynamics and the characteristic process disturbances. Pabedinskas et al (1994) have further developed a model for the free radical initiated PP degradation by reactive extrusion with combination of the kinetic model of the PP degradation reaction with a simplified model of the melting mechanism in the extruder. Experimental data of the molecular weight distribution (MWD) and average molecular weight (M_w) for the degraded PPs were first compared with the kinetic model alone and later with the combined kinetic-melting model. It was found that the kinetic-melting model provides significantly improved predictions compare to the original kinetic model.

Relationship between viscosity and molecular weight distribution (MWD) studied and then this correlation was used to find out the effect of initiator concentration on the degradation process. Weight average molecular weight (M_w) was predicted by the

combination of kinetic and melting model. The kinetic-melting model predicted properties can be used to significantly improve the performance of process control schemes for the degradation.

Tzoganakis et al (1988) developed PP degradation model by reactively extruding PP with 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane as a radical initiator. Modified materials were analysed in terms of melt flow index (MFI), flow curve, extrudate swell, and molecular weight distribution (MWD). The measured data were presented and correlations among various parameters were considered. A kinetic model was also proposed and experimental data were compared with data predicted from the model.

Azizi and Ghasemi (2004a) also studied controlled PP rheology by peroxide promoted degradation process. Melt flow index (MFI), mechanical, thermal and rheological properties were studied to evaluate the effect of initiator concentration and screw speed on these properties. It was concluded that, initiator concentration was the most significant variable. Melt flow index increased and viscosity decreased with initiator concentration. On the other hand, reaction temperature and screw speed had no significant effect on the melt flow index of the extrudate. Melting point remained almost same and crystalline fraction also had less effect of degradation process for all concentrations of peroxide. Elongation at break and impact strength reduced considerably at higher concentration of peroxide beyond 0.1 wt %.

2.4.1.2 Grafting and crosslinking of monomers onto polymers

Grafting monomers onto base polymers is one of the important reactive extrusion processes. This process produces a polymer with attached reactive functional group with better physical properties, improved polymer adhesion to mineral fillers, glass fibres, metals and other polymers. Polyolefins are generally modified by grafting reactions. Typically, peroxide is used with polyolefins. Peroxide attacked on the polyolefins backbone to abstract hydrogen atom and create free active radical which grafted with monomer. The monomer being grafted must have a reactive group, usually an unsaturated double bond. This is further reacted with the free active radical on the polymer chain. A second functional group on the monomer adds new properties to the grafted polymer. A typical commercial example of this process is grafting maleic anhydride (MAH) monomer to a polypropylene polymer.

Polance and Jayaraman (1995) investigated the mixing in reactive extrusion of low density polyethylene melts by comparing the melt flows of linear low-density polyethylene (LLDPE) and branched low-density polyethylene (LDPE) in a fully intermeshing co-rotating twin-screw extruder. The shear viscosity curves for LLDPE and LDPE were quite similar, but LDPE has a significantly higher apparent extensional viscosity over a wide range of stretch rates. Typical design of the fully intermeshing co-rotating twin screw extruder creates axial pressure gradients and provides a non-uniform geometry for axial flow in the mixing zone. Better axial dispersion was achieved for LLDPE which is attributed to the greater extensional viscosity of the LDPE. During the reactive extrusion process, solid maleic anhydride (MAH) and polyethylene were added at the feed port and the peroxide initiator was added directly to polymer melt. Residence time distributions measured for LLDPE melt indicate reduced levels of axial mixing with reaction. The reduction in mixing is due to a crosslinking reaction that occurs in parallel to the grafting reaction. This change in mixing was smaller than the difference in mixing between LDPE and LLDPE.

Kim and Kim (1993a) introduced the crosslinking of an isotactic PP in a twin-screw extruder. The whole samples of the products were characterized in terms of melt flow index, mechanical properties and differential scanning calorimetry (DSC). They found linear enhancement in melt flow index (MFI) with crosslinking. However, chain scission dominated crosslinking process resulted in decreased hardness, modulus and impact strength. Further these researchers used triacrylates type multifunctional monomer with/without peroxide. Modulus, yield strength and elongation improved while reduction in MFI reported. Finally, it was concluded that triacrylates were the most effective multifunctional monomer among the polyfunctional monomers used. Kim and Kim (1993b) also studied crosslinking of high density polyethylene by reactive extrusion using peroxide and co-agents, together and alone. They have studied the rheological, thermal and mechanical properties of the modified materials it was reported next the MFI decreased dramatically with peroxide, linearly with trimethylolpropanetriacrylate (TMPTA), but parabenzoquinone (PBQ) modification showed slight increase in MFI. Viscoelastic property improved more or less with all modifiers used. Impact strength was improved significantly with TMPTA.

Tang et al (1989) have reactively extruded LLDPE in a single screw extruder and in an extrusion plastometer using organic peroxide as a free radical source. Low peroxide

concentration was used before and then extended to high concentration for gel content assessment. Characterisation was done in terms of melt flow index (MFI), viscosity curve, extrudate die swell and gel content of the modified resin. MFI decreased linearly with peroxide content and all viscoelastic properties improved with peroxide modification. Gel content of 90% was observed with 0.1 wt% of peroxide used.

Venkatraman and Kleiner (1989) produced three types (thermochemical crosslinking using heat, using catalyst under moisture and using high-energy radiation) of crosslinked PE. Tensile behaviour at break, shear modulus, gel content, and crystallinity were measured for all modified samples. Distribution of crosslinks appears to be a major factor in mechanical properties and crystallinity. Degree of crystallinity experienced significant change because of this distribution. These distributions were reorganized on the basis of the mechanism of crosslinking and the resultant location of crosslink sites.

Lachtermacher and Rudin (1995a,b,1996a,b) reported reactive extrusion of LLDPE with low level of 2,5-dimethyl-2,5 di (t-butylperoxy) hexane in co-rotating intermeshing and counter rotating non-intermeshing twin screw extruder. In these series of publications they (Lachtermacher and Rudin, 1995a) observed long-chain branching and broad molecular weight distribution in size exclusion chromatography (SEC) analysis and this again reconfirmed by C- nuclear magnetic resonance (C-NMR) analysis. These results indicate that the major chain extension mechanism is an end-linking reaction between terminal vinyls or allylic radicals formed at chain ends and secondary radicals. These both types of radicals are formed by hydrogen abstraction. Moreover, changes in thermal behaviour were observed by differentiation scanning calorimetry (DSC). Viscoelastic property improvement of reactively extruded LLDPE was also observed (Lachtermacher and Rudin, 1995b). However, die swelling decreased as a function of peroxide concentration. In addition, elongation viscosity enhancement observed under both isothermal and cooling conditions, along with decrease in extensibility. Lachtermacher and Rudin (1996b) also observed similar molecular structure and rheological properties in the two different methods of peroxide addition in the first method; peroxide was added in the feed section and in the second, peroxide pumped into the melted polymer. Regardless of similarities in the molecular and rheological properties, second method was effective as low concentration of peroxide needed to conduct the reaction. Moreover, setup was more difficult in terms of its control and gel

fraction was observed. Overall, reactive extrusion processes critically depend on the methods of addition of peroxide and mixing conditions.

Suwanda and Balke (1993a) investigated the combined reactive extrusion of polyethylene and orientation implying melt pullers coupled with pair of rollers and balance. Polymer orientation in forms of other than fibres and films was carried out continuously with reactive extrusion. It was reported that, the effect of low initiator concentrations depend on the degree of branching, the molecular weight and its distribution and the degree of unsaturation of the polyethylene. The formation of branched molecules played an important role in enhancement of molecular weight and limited draw ratios attainable by the extrusion-orientation process. It was also found that a method involving the use of UV sensitizer and crosslinker followed by irradiation was directly adaptable to the above process and provided significant improvements in creep resistance.

Ganzeveld and Janssen (1992) investigated the effects of screw speed, temperature, initiator concentration and fully filled length of extruder on grafting of maleic anhydride (MAH) with high density polyethylene (HDPE). It was reported that it is better to use low percentage of MAH for grafting reaction. Higher percentages of MAH in the extruder led to the lower conversion and decrease in degree of grafting of MAH. Hence, it led to a non optimal reaction process. Screw speed increment resulted in both decrease in residence time and degree of grafting. On the other hand, degree of mixing increased due to screw speed increment and therefore mixing is necessary for high conversion. However, combining the two effects obviously results in an optimum value of overall conversion. An increased temperature of the barrel wall lead to more complete decomposition of the initiator and initiator's reaction constant increased. It led to more radical production resulting to a higher grafting percentage of MAH. The effect however was also limited. Rapid dissociation of the initiator caused the formation of many radicals at the same time. In addition, fully filled barrel of extruder bought about increased residence time and hence conversion.

In another publication, Ganzeveld and Janssen (1994) have analysed the role of mixing and rheology in reactive extrusion. Varying viscosity and amount of materials fed in the extruder to control the mixing process. The whole process was studied with a decolorization reaction in terms of influence on the mixing in the reaction process in

fully intermeshing counter rotating twin screw extruder with transparent barrel. Finally, it was concluded that, faster mixing depend on low viscous component and its amount present in the mixture. The experimental results agreed well with the theoretical analysis of the flow in the mixing zones of the extruder.

Wang et al (1994) have reactively extruded branched acrylic acid grafted polypropylenes with hexadecylamine. The authors reported formation of anhydride, imide and amide during reactive extrusion by Fourier transform infrared spectroscopy (FTIR) also un-reacted carboxylic acid was confirmed in FTIR spectra. Viscosity and viscoelastic properties improvement found with the increasing concentration of alkyl amine group. Wang et al (1996) also modified isotactic polypropylene with functional monomer pentaerythritol triacrylates and 2, 5-dimethyl-2, 5(t-butylperoxy) hexane peroxide in a reactive extrusion process. Thermal and rheological properties of the products reflected the presence of branching or crosslinking mechanism in the modified PP. Dagli et al (1991) have reviewed the effects of reactive extrusion variables on the characteristics of nylon6 and polypropylene blends with potential applications in recycling.

Mead (1995) has presented the system of the homogeneous and non-homogeneous reactive extrusion of polypropylene and developed a model using random chain scission statistics combined with the double reptation mixing rule. The behaviour of both the molecular weight distribution and linear viscoelastic material properties was quantitatively predicted for the reactive extrusion-palletization process.

2.5. ORGANIC PEROXIDE AS A CROSSLINKING AGENT – AN INTRODUCTION

It is very easy to modify the properties of polyethylene and other olefinic polymers by crosslinking under the action of a free radical generator, for example organic peroxide. Organic peroxides are versatile source of radicals that are formed after thermally induced homolysis of the peroxide bond. The major radical-molecule reactions are additions and SH_2 –reactions; e.g. H-abstraction, atom transfer, unimolecular reactions; e.g. β-scission. In synthesis reactions, undesired radical-radical reactions such as radical combination and disproportionation can be avoided by proper choice of the type of peroxide and reaction conditions. Table 2-1**Error! Reference source not found.** shows

crosslinking method for polyolefin modification and its effects on properties and applications.

Table 2-1 Modification of polyolefins and its characteristics and applications

Polymer	**LDPE, HDPE, EVA, EPM, EPDM,etc.**
Characteristics	• Decrease of MFI (Melt flow Index) • Increase of MW (Molecular weight) • Increase in Viscosity • Branched architecture
Main Applications	• Cable insulation (LDPE) • Pipes and vessels (HDPE) • Foamed articles (EVA) • Elastomers (EPDM , EPM)
Process	• Crosslinking • Silane crosslinking • Others (e.g. – Radiation, Sulphur)

2.5.1 Organic Peroxide Chemistry

Free radical crosslinking lead polyolefins to undergo three types of desired reactions and other side reaction eg. oxidation, degradation. These three reactions are crosslinking, chain scission and grafting reactions

A free radical reaction generally contains three types of reactants (1) polymer (2) unsaturated molecule (eg. vinyl monomer) and (3) free radical initiator. Typical free radical crosslinking reaction scheme is presented below (equations 2.1 to 2.5). Primary free radicals are generated by thermal decomposition of free radical initiator in the presence of monomer and the polymer (equation 2.1). It is necessary to have the same range of the decomposition temperature of the particular peroxide and processing temperature range of the polymer to carry out further desired reactions effectively (Perez et al., 2002). The thermal decomposition of organic peroxides is a first order reaction. Increase in temperature of about 10°C results in a 2-3-fold increase in

decomposition rate (Dorn, 1985). Primary free radicals then follow two completely different reaction pathways, one leading to undesired reaction while other leads to favourable reactions. Undesired reaction occurs rarely on the polymer backbone because a propagating monomer radical usually has a limited hydrogen capacity unless it is very reactive monomer. On the other hand, when the primary free radical reacts with the polymer and abstract hydrogen atom from the polymer backbone (equation 2.2) and thus forms a free macro radical. This free macro radical can have three types of desired reactions based on the nature of the macro radical and the type of the corresponding polymer backbone.

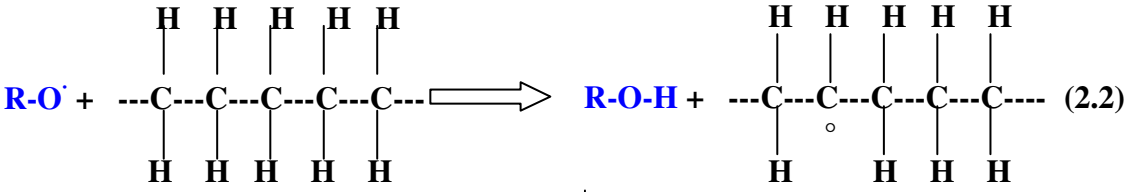
2.5.1.1. Chain Scission

A macro radical can be highly unstable and the chemical bond (C—C bonds) at any location or near the macro radical may break down to two smaller fragments. This called chain scission or degradation (equation 2.4). This process causes a reduction in molecular weight. Molecular weight distribution narrows as chain scission proceeds. Reduction in molecular weight causes increase in melt flow index and thus decreasing melt viscosity. An important commercial application of the use of controlled chain degradation is in the production of controlled rheology polypropylene (Pabedinskas and Cluett, 1994, Tzoganakis et al., 1988).

- **Free Radical Formation**

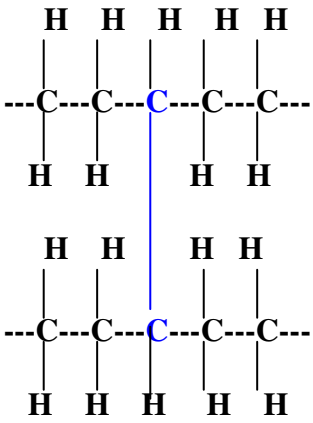
(2.1)

- **Hydrogen Abstraction**



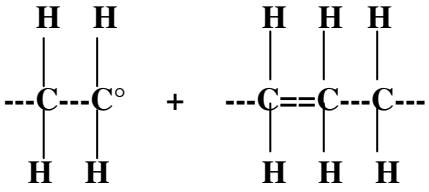
(2.2)

- **Crosslinking Reaction**



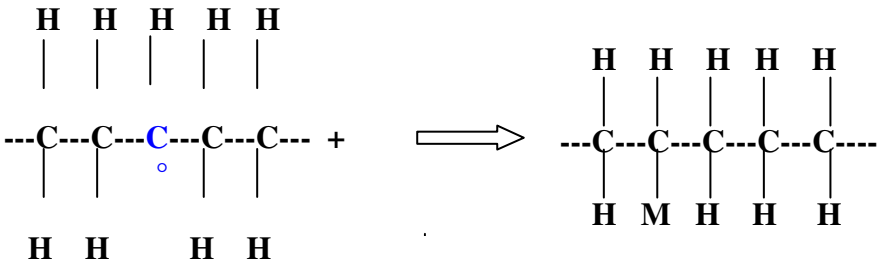
(2.3)

- **Chain Scission Reaction**



(2.4)

- **Grafting Reaction**



(2.5)

Graft Polymer
M = Monomer For example vinyl monomer

2.5.1.2. *Branching and crosslinking*

Macromolecules experience bimolecular termination by combination of two or more macro free radicals and result in long chain branching (equation 2.3). Broadening of this long chain branching process forms three-dimensional network called crosslinking. The formations of high molecular weight chains via long chain branching increases melt strength, die swelling and enhance strain hardening properties. High melt strength and good strain hardening properties are particularly important in thin film applications. Sugimoto et al (1999) produced long chain branched polypropylene with introduction of organic peroxide and reported enhancement of melt strength. However, crosslinking is often considered undesirable but sometimes it may also bring property enhancement such as service temperature, solvent resistance, flexural modulus and dimension stability. Perez et al (2002) modified four type of high density polyethylene with 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-hexane peroxide. The main feature of this study was to analyse the effect of vinyl-content of the crosslinking degree and corresponding property improvement. They reported molecular weight enhancement hence broad molecular weight distribution (MWD). Strong viscoelastic property improvement was also observed with vinyl containing polymers.

Probability of crosslinking or long chain branching is higher in the polyethylene than in the polypropylene because polyethylene's secondary-carbon-centred macro radical is very reactive to couple with another macro radical results in a branched or crosslinked polymer. On the other hand, polypropylene tends to fragment to a secondary-carbon-centred radical and a smaller unsaturated segment by β-scission. Therefore, polyethylenes have greater ability to from long chain branching or crosslinking. Polypropylene has tertiary-carbon-centred macro radical which less reactive than secondary-carbon-centred macro radical of polyethylenes. Hence, the probability of polypropylene molecules to form long chian branches is lower then polyethylenes. In other words, PP molecules are more suspected to chain scission with peroxide.

2.5.1.3. *Grafting*

Macro radical reacts with the double bond of the vinyl monomer, forming a branched macro radical is called grafting reaction (equation 2.5). If this formed macro radical continues to react with other monomer molecules, it will lead to longer chain molecules. This process is responsible for polymer property improvement. Ganzeveld and Janssen

(1992) reported grafting of maleic anhydride (MAH) with high density polyethylene (HDPE). According to Gazeveld and Janssen (1992), low concentration of MAH is desirable for the grafting reaction and property improvement. They also studied the effects of screw speed, temperature, initiator concentration and fully filled length of grafting of MAH onto HDPE. For more discussion see section 2.4.1.2.

2.5.2 Selection Criteria of Organic Peroxide as a Crosslinking Agent

Organic peroxides (free radical initiators) are sources of the grafting and crosslinking. Organic peroxide can create free radicals by the homolytic cleavage of the given oxygen-oxygen bond of the peroxide in the decomposition temperature range of the particular peroxide. Decomposition product contains un-paired electrons which are intermediates and very reactive with short lifetimes. According to the overall crosslinking and grafting reaction, the only suitable peroxides are those of which the primary free radicals should be sufficiently reactive to abstract hydrogen atoms from the polymer chain to form the corresponding macro free radicals. Selection of proper initiator for a given process depends on reaction conditions and the reactivity. Criteria for selecting a suitable peroxide for given crosslinking or grafting process is

(a) Half life
(b) Initiator crosslinking capacity
(c) Hydrogen abstracting capacity

These all criteria's are explained in detail in the following section

2.5.2.1 Half Life

The half life of peroxide ($t_{1/2}$) is a measure of its rate of decomposition at a certain temperature and other given conditions. It gives the indication of the time when half of the peroxide consumed or decomposed. In addition, the higher the decomposition rate, the lower the half life. Half life is very important factor for crosslinking reactions. Decomposition reaction is a first order reaction as shown below.

$$-\frac{dc}{dt} = kC \qquad \textbf{(2.6)}$$

$$t = \ln\frac{c_o}{c_t}k \qquad \textbf{(2.7)}$$

$$t_{1/2} = \ln\frac{2}{k} \quad \textbf{(2.8)}$$

$$k = k_0 \exp(-\frac{\Delta E}{RT}) \quad \textbf{(2.9)}$$

$$t_{1/2} = \ln(\frac{2}{k_0})\exp(\frac{\Delta E}{RT}) \quad \textbf{(2.10)}$$

Where, k= rate constant, k_0= Collision Factor, R=Gas Constant T= Temperature
ΔE= Activation Energy $t_{½}$=Half Life

Half life of particular peroxide depends on rate constant k as in the above equation. Rate constant (k) depends on the relative stability of the formed radicals, steric factor and electron effects (Al-Malaika, 1997). Temperature dependence of the half life can be represented by Arrhenius equation (equation 2.10) by substituting equation 2.9 into equation 2.8. Collision factor (k_0) is included with these (relative stability of the formed radical, steric factor, electron effect) all factors in the Arrhenius equation. According to the Arrhenius type equation, increase in temperature of about 10°C results in a 2-3-fold increase in decomposition rate. Moreover, activation energy is the controlled factor for the decomposition rate and hence the half life time. The half life of peroxide also depends on peroxide concentration because of induced decomposition (when formed free radical itself attack and help in decomposition cause induced decomposition) (Al-Malaika, 1997). Moreover, the half life is also dependent on pressure. However, pressure has much smaller effect on the half life of peroxide.

2.5.2.2 Initiator crosslinking efficiency

The initiator crosslinking efficiency is defined as the fraction of primary radicals which abstract hydrogen atoms from the polymer backbone forming the corresponding macro free radicals. It is very desirable to have more crosslinking efficiency of the initiator. Reaction of decomposed primary radicals from initiator with monomer is an undesired reaction because in this case there will be less primary radicals available for hydrogen abstraction. Thus, initiator polymerisation efficiency is inversely propositional to the initiator crosslinking efficiency.

2.5.2.3 Hydrogen abstracting capacity

Hydrogen abstracting capacity depends on nature of the primary radicals and type of the carbon-hydrogen bond (C-H) which is related with chemical structure of hydrocarbons. Evans-Polanyi relation (equation 2.11) relates the activation energy (ΔE) to the total enthalpy change ΔH° as shown in the following equation.

$$\Delta E = \alpha \Delta H^{\circ} + C \qquad \textbf{(2.11)}$$

Where α and C are constants

ΔH° = Difference between the dissociation energy of the bond being broken and that of the bond being formed.

According to this theory, lower dissociations energy means it is easy to abstract hydrogen atoms and lower the activation energy for hydrogen abstraction. Moreover, atoms containing lower dissociation energy have low reactivity and higher stability of the free radical formed from hydrogen abstraction, which is not desirable.

2.6. EFFECT OF BRANCHING ON POLYMER PROPERTIES

Commercial branched polymers usually neither have branches of equal length, nor have perfectly randomly structured branching because the manufacturing conditions are often biased rather than completely random. However, star and comb branched polymers have branches of equal length. In practice, it has been widely accepted that long chain branches (LCB) are usually of the same order of length as the main chain while short chain branches (SCB) are of a size up to that of only a few repeating units. SCB influences the morphology and solid state properties of semicrystalline polymers, whereas LCB has a remarkable effect on solution viscosity and melt rheology.

The universal method for the determination of long side chains in a polymer assumes that the branched molecule has a smaller coi1 dimension than a linear molecule of the same molecular weight and the same chemical composition (Schröder et al., 1982). The branching index (g') is a measure of the amount of branching in the polymer. It is defined as the ratio of intrinsic viscosities of the branched and linear polymers of the same molecular weight.

The most documented commercial polymer in terms of branching is branched polyethylenes (PE). GPC (gel permeation chromatography), C-NMR (nuclear magnetic resonance) and FTIR (Fourier transform infrared spectroscopy) methods have been used to measure the amount of branching. For PE, most GPC calculations assume that the polymer is randomly branched and it contains tri-functional branching points (Pang and Rudin, 1993). Although many techniques have been developed to characterize branched polymers, rheological measurements often provide better alternatives for assessing the extent of branching in polymers.

Viscoelastic properties (properties of both a viscous liquid and an elastic solid) are the most important rheological feature of the polymer. Rheological properties of the polymer have considerable practical value in processability. The complete rheological description provides important information about both viscosity and elasticity. The ratio of the shear stress applied on the fluid to shear rate which measure the change in shape under internal friction is called shear viscosity. Elasticity is termed as resistance to the change of shape of a solid material. Viscosity dependence on the shear rate of the fluid is generally illustrated by a plot of log (melt viscosity) versus log (shear rate). Another term which is well described by rheology is the elongation or extensional viscosity which is similar measure of resistance to a change of shape of a fluid under normal stresses. Elongation viscosity plays an important role where drawing and spinning are involved.

It is generally accepted that, the different rheological properties are outcome of different molecular structures possessed by different materials such as weight average molecular weight (Mw), molecular weight distribution (MWD) and molecular orientation like long chain branching. Rheology is used as a structural tool to define polymer structure like nature and degree of LCB. Effects of molecular behaviour on the rheological properties have been reported by some researchers (Rochefort et al., 1979, Rachapudy et al., 1979, Raju et al., 1979) in terms of model (star branched) which contain well-defined branch frequency, branch length, and narrow MWD. However, as a limitation of these model systems; molecular orientation and hence viscoelastic properties in case of commercial branched polymers may not be well presented (Bersted et al., 1981).

Generally, an increase in molecular weight results in increase in shear viscosity, elongational viscosity and elasticity. Moreover, the low shear rate viscosities of broad MWD samples are higher than those of narrow MWD samples (Guillet et al., 1965). Moreover, shear viscosity decreases at high shear rate as MWD broadens. Elongational viscosity change is similar to the change in shear viscosity with change in MWD. Following is a brief summary on the effects of branching on the rheological and other properties of polymers.

2.6.1. Shear and extensional viscosity

Extensive studies have been done on the rheology of polyolefins (Bersted, 1985, Lem and Han, 1982, Tang et al., 1989, Ghosh et al., 1997, Tian et al., 2006) modified by organic peroxides in order to produce extended chain mechanism. Bersted et al (1981) and Bersted (1985) reported spectacular increase in low shear rate viscosity with increase in branching introduced by both blending of LDPE/HDPE (Bersted et al., 1981) because of an increased concentration of the more viscous branched component and peroxide decomposition (Bersted, 1985). However, shear viscosity is decreased at high shear rates. These observations were continuation of the work done on effects of branching on shear viscosity of polymers by Graessely and co-workers (Rachapudy et al., 1979, Raju et al., 1979, Rochefort et al., 1979) with mono-dispersed linear and star branched polybutadienes. Zero shear viscosity enhancement was observed by Janzen and Colby (1999) with increase in degree of branching when modification was done by even low level of peroxide.

Numerous studies of star polymers have been reported in the literature. Raju et al (1979) have observed an increase in zero shear viscosity of a branched polymer over that of a linear polymer of equivalent molecular size for stars of polyisoprene and hydrogenated polybutadiene (HPB). Raju et al (1979) also reported close relationalship between zero shear viscosity and molecular weight of the branched chains in the polymer. They reported that the zero shear viscosity increased with increase in molecular weight of the branches. Carella et al (1986) and Fetters et al (1993) confirmed this finding. Other publication of Graessley and Raju (1984) studied blends of linear and star branched hydrogenated polybutadiene (HPB). Both constituents had similar zero shear viscosities and different molecular weight. Star branched material reveals higher viscosity. The zero shear viscosities of the blends were not less than those of the pure components.

The authors interpreted from this observed behaviour that the viscosity enhancement does not depend on the interaction between two branched molecules but rather on the interaction of a branched chain with other entangled chains.

Roovers (1984) studied the linear viscoelastic behaviour of H-shaped polystyrenes. He reported higher degree of viscosity enhancement of H-shaped polymers than three and four arm star polymers having same molecular size. Kasehagen et al (1996) have reported the rheological behaviour of randomly branched polybutadienes produced by adding increasing numbers of branches to two essentially mono-disperse polybutadiene precursors. They reported broadening of the relaxation mechanism with enhancement of long chain branching. They also found that the zero shear viscosity increased with LCB.

Wood-Adams et al (2000) reported four main effects of long chain branching on the complex viscosity: (1) the zero shear viscosity is increased for the polymers having same molecular weight, (2) the amount of shear thinning is increased, (3) the transition zone between the zero shear viscosity and the power law zone is broadened, and (4) two points of inflection appear within the transition zone.

Therefore, branching can either increase or decrease zero shear viscosity depending on the length of the branches. LCB usually increases the shear viscosity at low shear rates, but decreases the viscosity at high shear rates.

Branching also has great influence on elongational viscosity and hence, strain hardening. For example, Gotsis et al (2004a) reported monotonic growth in elongational viscosity of polypropylene initially but with the peroxide modification, accelerated growth in viscosity and initial slope was reported. This region is called as strain hardening region. Generally, elongational viscosity of the linear PP grades was non-strain hardening. Peroxide modification of PP results in long chain branching. Branching increased the possibility of entanglements in the melt and reduced the rate of disentanglement. Thus, the modified polymers showed enhanced strain hardening in uniaxial elongational flow. Nakajima and Harrell (1982) also showed that the strain hardening is the result of increased chain entanglement due to long chain branches. In general, the more branches added on the chains, the higher the strain hardening. Mantia et al (1986) also reported enhancement in elongational viscosity with increase in branching points.

2.6.2. Viscoelastic properties

Nakajima and Harrell (1982) found that the solution concentration dependence of viscoelastic properties was significantly affected by the presence of long chain branches. Perez et al (2002) reported progressive increase in elastic modulus (G'), viscous modulus (G") and dynamic viscosity (η') with increase in amount of peroxide in the process of peroxide modification of high density polyethylene (HDPE). Formation of larger macromolecules by chain linking reaction results in viscoelastic property enhancement (Bersted, 1985, Ghosh et al., 1997, Lem and Han, 1982). Time temperature superposition (TTS) was employed to obtain master curves of storage modulus (G'), loss modulus (G") and complex viscosity (η*). Viscous and elastic response was enhanced by long chain branching. A modified Cole-Cole plot (log G' Vs log G") was used for assessment of molecular architecture. Changes in the shape and displacement of the curve give an indication of changes in branching architecture. This method is very useful to evaluate materials with similar molecular weight distributions but different molecular architectures.

2.6.3. Viscous flow activation energy

Generally, branched polymer has higher flow activation energy. For example, Parez et al (2002) found higher flow activation energy with higher amount of peroxide and hence higher amount of branching mechanism. Raju et al (1979) showed that the flow activation energy for star branched hydrogenated polybutadienes is primarily a function of branch length. Romanini et al (1980) reported that long-chain branched LDPE have higher flow activation energy than that of linear PE. Bersted (1985) also observed that the very low levels of LCB in PE increase both flow activation energy and viscosity at low rates and that the flow activation energy increases with branching level**.** Laun (1936) also suggested that long chain branches are responsible for the high flow activation energy of LDPE compared to HDPE, and a growing number of the branches increase the flow activation energy.

2.6.4. Molecular properties

Molecular weight and its distribution is one of the criteria to evaluate branching mechanism in the polymer. A polymer containing a broad range of chain length is said to have a broad molecular weight distribution (MWD). These types of resin comprise good environmental stress cracking resistance (ESCR), good impact strength and better

processability. Perez et al (2002) observed increase in weight average molecular weight (Mw) and broaden the molecular weight distribution and it shifted towards high molecular weight when four different types of high density polyethylene are reacted with organic peroxide. Lem and Han (1982) worked on the modification of LDPE and HDPE with the use of dicumyl peroxide with the aim of introducing branching and found increase in number average (Mn) and weight average molecular weight (Mw) as well as broad molecular weight distribution (MWD). Wood-Adams et al (2000) used triple-detector method in the gel permeation chromatography (GPC) to evaluate long chain branching in the polymers. Triple-detector GPC can measure intrinsic viscosity and molecular weight for each fraction of the polymer simultaneously and independently. Plot of double-logarithmic intrinsic viscosity versus molecular weight can generate entire molecular weight distribution for any given sample. This plot is called as "Mark-Houwink plot". They used this plot with Mark-Houwink and Zimm-Stockmayer relations and found that the distribution curve intersect the curve for the linear sample and got large deviation in the high molecular weight region of the distribution.

2.6.5. Other properties

Degree of crystallinity has been reported to decrease with extended long chain branching. For example, Venkatraman and Kleiner (1989) measured thermal properties using Perkin-Elmer DSC for three types (peroxide modification, irradiation method and humidity cured crosslinking) of crosslinked polyethylenes. The authors observed decrease in degree of crystallinity with the extent of crosslinking in first and second heating cycle. Decrease in crystallinity was due to the restriction of the chain mobility which is the result of long chain branching. However, humidity cured sample's crystallinity was independent of crosslinking during second heating cycle. They also found decrease in tensile stress at break with crosslinked material. Moreover, peroxide modified samples showed increase in melting point temperature and decrease in heat of fusion (Kim and Kim, 1993b). Kim and Kim (1993b) also measured mechanical properties of the modified samples. The most significant improvement was observed in the impact strength. Hardness was almost independent of peroxide modification. Flexural modulus and yield strength also increased with peroxide induced crosslinking. However, elongation at break dropped dramatically with peroxide addition.

2.7. CONCLUDING REMARKS

Polymer recycling is rapidly becoming important area of polymer engineering. Property improvement is the main concern of the recycled plastics. Contamination and poor mechanical properties of the recycled plastics decreased attention of the industries toward its use in first grade applications. It has been shown by different researchers that the blending of virgin material can result in changes of morphology, rheology and mechanical properties. Introduction of filler or free radical initiator can also modify the rheological and molecular properties. Different types of filler and free radical initiators have been used so far along with different type of processes. In general, attempts have been made towards improvement of recycled material properties despite its limitations in various applications.

High density polyethylene from post consumer recycled milk bottles can be used for blow moulding and non pressure drainage piping application after recycling. As previously mentioned, blending, filler and free radical initiator can be used to recycle milk bottle plastic. Melt strength and environmental stress cracking resistant are the main properties of the recycled material while using as blow moulding parts and piping. In general, three methods have been employed to improve properties of the recycled HDPE.

- Blending with virgin material.
- Introduction of filler.
- Introduction of free radical initiator.

Although literature review indicates that blending and free radical initiator technique have been widely studied, very little work has been reported on melt strength improvement and effect of branching mechanism on molecular properties and morphology of recycled HDPE. In addition, very little work has been carried out to identify the suitability of these materials to use for piping applications.

This work will provide a better understanding of melt strength and shear rheological behaviour of recycled HDPE resin modified by small amount of free radical initiator through reactive extrusion. Furthermore, this work will investigate a relationship between rheology and molecular properties. An attempt has been made to predict the environmental stress cracking resistant of the modified material.

CHAPTER 3. MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES

This section summarizes methods for material preparations and characterizations of virgin and recycled high density polyethylene modified by organic peroxides. Material preparations include reactive extrusion of these two materials with two different organic peroxides in a laboratory scale twin screw extruder. Material characterizations include

3. Dynamic and steady shear rheological measurement.
4. Melt strength measurements.
5. Molecular characterisation using gel permeation chromatography (GPC).
6. Morphological characterisation using modulated differential scanning calorimetry (MDSC).
7. Tensile testing using Instron universal testing machine.
8. Environmental stress cracking resistance (ESCR) testing.

3.1. MATERIALS

The materials used in the production of high melt strength recycled HDPE are divided into two classes as below

1. Virgin HDPE (HD5148).
2. Post consumer recycled HDPE.
3. Organic peroxides.

3.1.1. Virgin High Density Polyethylene (V-HDPE) homopolymer

The virgin high density polyethylene (grade HD5148) used in this project was supplied by Qenos Private Limited, (Australia). HD5148 grade is premium quality resin exclusively designed for use in high speed reciprocating screw moulders. Moreover, this grade is used for food contact applications according to AS2070-1999 and relevant FDA regulations. This product meets requirements FDA 21 CFR 177.1520 (c) 2.1 and AS2070 section 4.1.1(a). However, this grade is not used for holding food during cooking without the required compliance testing. Table 3-1 gives the properties of this material. High density polyethylene is generally produced by Ziegler-Natta vinyl polymerization process. It is used in manufacturing of milk bottles, cream container, fruit juice and cordial bottles.

3.1.2. Recycled High Density Polyethylene (R-HDPE)

Post consumer recycled high density polyethylene was obtained from Visy plastics private limited (Australia). This material is composed of disposed milk bottles and other small blow moulding containers. Collection process to production of recycled resin is mentioned in the second chapter. Properties of this resin are mentioned in Table 3-1, together with virgin HDPE (HD5148).

One of the proposed uses of recycled HDPE resin is low pressure pipe for drainage and other applications. Stress cracking resistance is one of the most important properties of this material so it can be used for low pressure pipe applications. It has been observed that the potential for HDPE milk bottle recovery and recycling has not been reached. The production of rural pipe provides another end market for these milk bottles ultimately contributing to landfill diversion. This project should increase markets for post-consumer HDPE dairy grade resin in low pressure and non-pressure pipe applications.

Table 3-1 Properties of two different HDPE

Properties	HD5148	R-HDPE
Specific gravity (kg/m3)	0.960	0.960
Melt index @ 190°C, 2.16 kg	0.80	0.60
Tensile strength at yield (MPa)	28	-
Elongation at break (%)	600	-
Melting point (°C)	120-135	120-135
Mw	100916	89814
Polydispersity	2.16	2.25
Additives	0-2 %	Carbon Black

Note: The information on HD5148 grade was obtained from QENOS website (www.qenos.com.au) and that of R-HDPE was obtained from data sheet supplied by Visy Industries. Molecular properties were obtained from GPC (gel permeation chromatography).

3.1.3. Organic Peroxides (OP)

Two organic peroxides Dicumyl peroxide (Figure 3-1) and 1, 3 1, 4 Bis (tert-butylperoxyisopropyl) Benzene (Figure 3-2) were obtained from Akzo Nobel Polymer Chemicals (Netherlands). Properties of the both peroxides are summarised below in Table 3-2.

Table 3-2 Properties of organic peroxides.

	Dicumyl Peroxide Luperox® DC	**1, 3 1, 4 Bis (tert-butylperoxyisopropyl) Benzene Luperox® F**
Molecular Weight	270.4	338.5
Active Oxygen content	5.92%	9.45%
Safe processing Temperature (°C)	135	135
Typical crosslinking Temperature (°C)	170	175

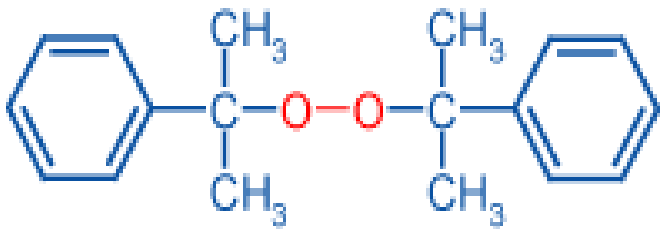


Figure 3-1 Chemical formula of Dicumyl peroxide
(www.specialchem4polymer.com)

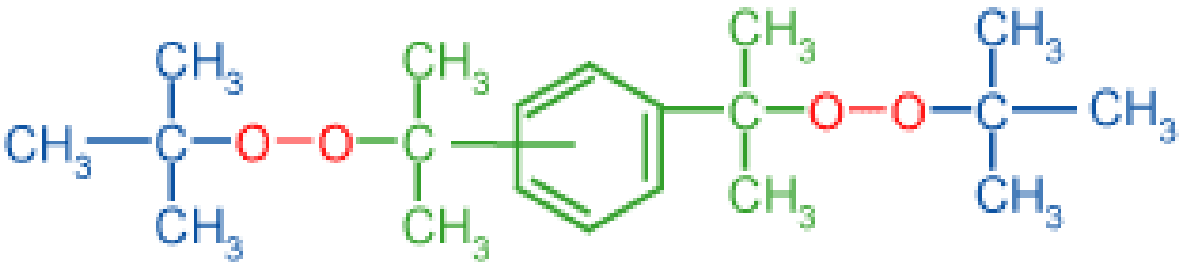


Figure 3-2 Chemical formula of 1, 3 1, 4 Bis (tert- butylperoxyisopropyl) Benzene
(www.specialchem4polymer.com)

3.1.4. Preparation of Peroxide Modified Samples by Reactive Extrusion

The series of organic peroxide modified virgin and recycled HDPE samples were prepared by reactive extrusion. Virgin or recycled HDPE was premixed with respective organic peroxide. This step involved a through mixing of particular proportion of virgin or recycled HDPE with organic peroxide. The premixing was carried out in a non sticky sealed polymer bag from both sides. This premixing is very important to mix the HDPE pellets and small quantities (0.02 wt%, 0.05 wt%, 0.07 wt%, 0.10 wt%, and 0.15 wt %) of peroxides thoroughly. For each concentration of peroxides (0.02 wt%, 0.05 wt%, 0.07 wt%, 0.10 wt%, and 0.15 wt %), samples were prepared. Details of samples prepared are shown in table 3-3.

Table 3-3 Details of compositions produced

wt% of V- HDPE or R-HDPE	wt% of DCP or OP2	Sample Name
100 V-HDPE	0.0 wt%	V-HDPE
100 V-HDPE	0.02 wt% DCP	V-HDPE+0.02% DCP
100 V-HDPE	0.05 wt% DCP	V-HDPE+0.05% DCP
100 V-HDPE	0.07 wt% DCP	V-HDPE+0.07% DCP
100 V-HDPE	0.10 wt% DCP	V-HDPE+0.10% DCP
100 V-HDPE	0.15 wt% DCP	V-HDPE+0.15% DCP
100 V-HDPE	0.02 wt% OP2	V-HDPE+0.02% OP2
100 V-HDPE	0.05 wt% OP2	V-HDPE+0.05% OP2
100 V-HDPE	0.07 wt% OP2	V-HDPE+0.07% OP2
100 V-HDPE	0.10 wt% OP2	V-HDPE+0.10% OP2
100 V-HDPE	0.15 wt% OP2	V-HDPE+0.15% OP2
100 R-HDPE	0.0 wt%	R-HDPE
100 R-HDPE	0.02 wt% DCP	R-HDPE+0.02% DCP
100 R-HDPE	0.05 wt% DCP	R-HDPE+0.05% DCP
100 R-HDPE	0.07 wt% DCP	R-HDPE+0.07% DCP
100 R-HDPE	0.10 wt% DCP	R-HDPE+0.10% DCP
100 R-HDPE	0.15 wt% DCP	R-HDPE+0.15% DCP
100 R-HDPE	0.02 wt% OP2	R-HDPE+0.02% OP2
100 R-HDPE	0.05 wt% OP2	R-HDPE+0.05% OP2
100 R-HDPE	0.07 wt% OP2	R-HDPE+0.07% OP2
100 R-HDPE	0.10 wt% OP2	R-HDPE+0.10% OP2
100 R-HDPE	0.15 wt% OP2	R-HDPE+0.15% OP2

The premixed virgin or recycled HDPE and peroxide was then reactively extruded by introducing it into a Brabender twin-screw extruder. The operation temperature of the extruder was maintained at 160 °C, 190 °C and 190°C from hopper to die section of the extruder. Screw speed of 75 rpm was used for the decomposition and crosslinking/branching between peroxide and HDPE resin. The mixing and residence time was approximately 4-5 minutes for all the compositions prepared. Air-cooling was provided to maintain the temperature of the barrel wall at 190 °C to avoid viscous

heating during the extrusion process. Moreover, crosslinking reaction is exothermic reaction (Ghasemi and Morshedian, 2003) so heat removal was done by water cooling method. The twin-screw extruder was used as a CSTR (continuous stir tank reactor) and the gap between the screws termed as plug flow reactor so series of plug flow reactors can give better reaction efficiency. On top of that, twin screw extruder can provide better dispersive and distributive mixing. In addition, high shearing is provided by counter-rotating screws and it is self-cleaning too. The L/D ratio is 7 with the screw having diameter of 41.8 mm. The screws are standard screws with axial grooves having width and depth of 5 mm. Optimum screw speed is desirable for good shearing force and mixing of organic peroxide with HDPE resin. However, higher shearing force results in polymer degradation. Residence time at 75-rpm speed was approximately 110 seconds. Short residence time is not desirable for decomposition and crosslinking reaction. Thus material was palletised and put through the extruder two times to complete the crosslinking reaction and total decomposition of the peroxides. Intensive care was taken to avoid the degradation of the material during reactive extrusion. Brabender twin-screw extruder is shown in figure below (figure 3-3). Final extrudate product was palletised and these pellets were used for various characterisations such as rheology, melt strength, modulated differential scanning calorimetry (MDSC), gel permeation chromatography (GPC) etc.

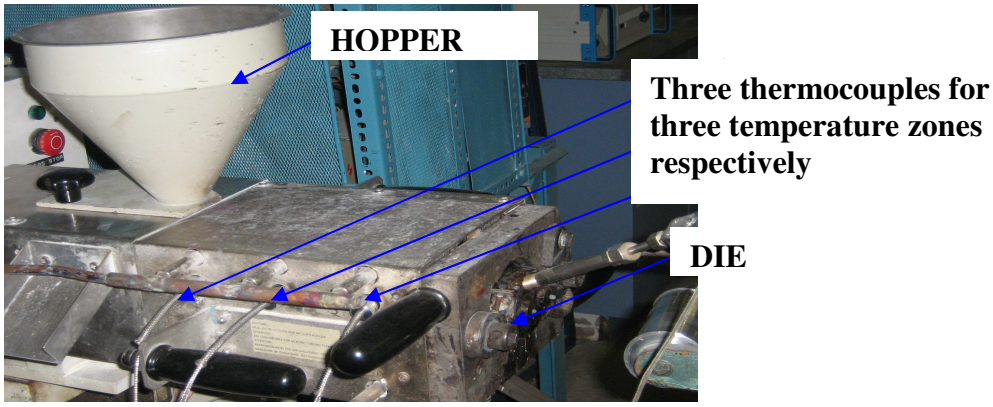


Figure 3-3 Brabender twin-screw extruder with three temperature zones from hopper to die

3.1.5. Sample preparation using compression moulding

Sample for rheological measurement were prepared on the compression moulding press. The compression moulded press was operated at 190 °C. Pellets were allowed to melt completely and then compression moulded for five minutes at 120 kN (27000 lbs) pressure, followed by cooling to 50°C within 7 minutes@ cooling rate of 20-30° C/min. These plaques were also used for rheological measurements. Care was taken to avoid degradation as well as bubble formation within the plaque. Compression moulding press is shown in figure 3-4.

Figure 3-4 Compression moulding machine equipped with separate temperature indicators for both plates and cooling lines.

3.2. CHARACTERISATION OF OP TREATED V-HDPE AND R-HDPE

Characterisation of the organic peroxide modified V-HDPE and R-HDPE in terms of rheological, molecular and mechanical properties is an important part of this project. This characterisation can help to know whether organic peroxide modified HDPE was still linear, branched or crosslinked. Following techniques were used to evaluate the effect of peroxide modification on virgin and recycled HDPE.

1. Gel permeation chromatography (GPC)
2. Modulated differential scanning calorimetry (MDSC)
3. Advanced rheometric expansion system (ARES)
4. Göttfert Rheotens melt strength tester.

5. Tensile testing using Instron universal testing machine
6. Environmental stress cracking resistance (ESCR) testing.

3.2.1. Rheological Measurements

Rheological measurements can be divided into two parts.

- Shear rheological characterisation.
- Uniaxial melt extensional measurement (melt strength).

These two types of rheological measurements would reveal the material's response towards different types of deformations and melt processing characteristics. This characterisation would give information about microstructure of these modified materials.

3.2.1.1 Shear Rheology

Shear rheological characterisation can be subdivided into dynamic (oscillatory) and steady shear based on the movements of the parallel plate in the advanced rheometric expansion system (ARES) (figure 3-5). All measurements were recorded and analysed using Rheometrics Rhios V4.0 software. 25 mm diameter parallel plates were used.

Figure 3-5 Rheometric Advanced Expansion System (ARES) equipped with Rheometrics Rhio V4.0 software.

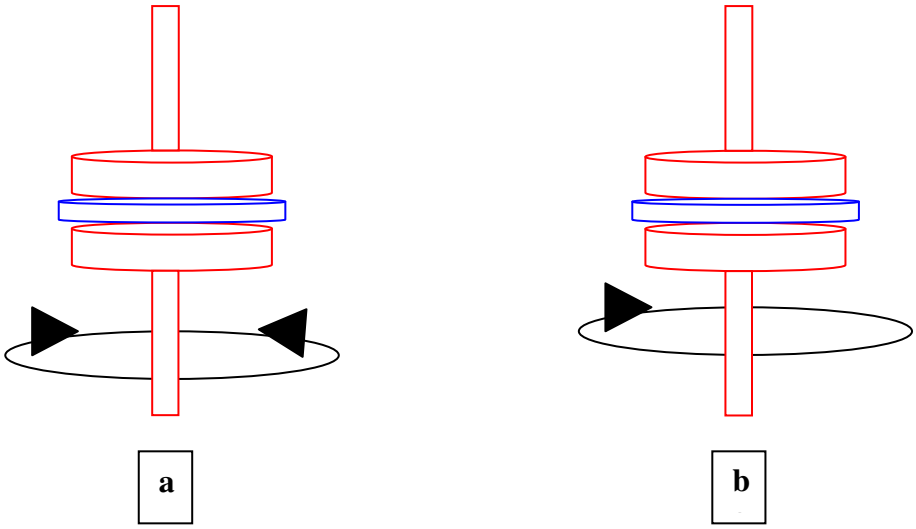


Figure 3-6 Schematic diagram of parallel plate geometry (a) Oscillatory motion of lower plate in the dynamic shear tests (b) Steady shear tests conducted by rotational motion of the lower plate

Figure 3-6 shows two modes of operations (a) oscillatory shear and (b) steady shear. These tests were being done with a force transducer with a range of 0.2 to 2000 g-cm torques. The 2 mm thick plaques from compression moulding were cut into 25mm diameter circular discs. System temperature should be in equilibrium before loading each sample. All tests were performed at 190 °C. Samples were placed between two plates when system reaches desired melting temperature. Gap between two plates were kept 2 mm after loading each sample. Dynamic frequency test were conducted with the step of determining the linear viscoelastic region (dynamic strain sweep) followed by dynamic frequency sweep. Dynamic frequency sweep tests were performed at frequencies in the range of 100 to 0.01 rad-s^{-1}.

In the parallel plate geometry,

H = Height between two plates when samples are loaded.

Ω = Constant angular velocity oscillation (dynamic shear test) or rotation (steady shear test) of the lower plate.

T = torque was measure by upper plate which is stationary.

(N_1 and N_2) = Normal stress function which are also measured by upper plate.

With all these parameters Powell (1998), Macosko (1994) and Morrison (2001) described the derivation of the shear viscosity and normal stress function (equations 3.1 and 3.2).

$$\eta\left(\dot{\gamma}\right) = \frac{T}{2\pi R^3 \dot{\gamma}_R}\left(3 + \frac{d\ln T}{d\ln \dot{\gamma}_R}\right) \quad \textbf{(3.1)}$$

$$N_1\left(\dot{\gamma}_R\right) - N_2\left(\dot{\gamma}_R\right) = \frac{2F}{\pi R^2}\left(1 + \frac{1}{2}\frac{d\ln F}{d\ln \dot{\gamma}_R}\right) \quad \textbf{(3.2)}$$

Where,

$\eta(\dot{\gamma})$ = Steady shear viscosity based on the perimeter of the plates.

R = Radius of the plate.

γ_R = Shear rate based on the plate perimeter.

F = Normal force

It is very difficult to maintain constant shear rate throughout the sample due to the variation in shear rate along the plate (Macky, 1998). This shear rate is called radial position dependent shear rate (apparent shear rate). This apparent shear rate can be calculated by following equation (equation 3.3).

$$\dot{\gamma}_R = \frac{\Omega R}{h} \quad \textbf{(3.3)}$$

Morrison (2001) reported usefulness of parallel plate geometry with small-amplitude oscillatory shear (SAOS). He derived two material functions η' (dynamic viscosity) (equation 3.4) and η" (out of phase complex viscosity (η*))(equation 3.5), which can be related to measured torque and phase leg (δ).

$$\eta'(\omega) = \frac{2hT\sin\delta}{\pi R^4 \omega \theta_0} \quad \textbf{(3.4)}$$

$$\eta''(\omega) = \frac{2hT\cos\delta}{\pi R^4 \omega \theta_0} \quad \textbf{(3.5)}$$

ϕ_0 = Flow direction of the sample.

Dynamic test consists of determination of linear viscoelastic region (dynamic strain sweep) followed by dynamic frequency sweeps. It is important to note that the measurements were performed within the linear viscoelastic region. The viscoelastic shear properties of the polymers were studied by measuring the storage modulus (G'), loss modulus *(G")* and the complex viscosity (η*) within the linear viscoelastic region of the polymers. The storage modulus measures the elastic response of a polymer while the loss modulus measures the energy dissipated during flow deformation.

3.2.1.2 Uniaxial Melt Extensional Measurements (Melt Strength)

There are three types of extension deformation involved with the polymer which is uniaxial, biaxial and planer. In this study, uniaxial extensional deformations of organic peroxide modified virgin and recycled HDPE were conducted and analysed. Uniaxial extensional rheological characterisation is very important in simulating the industrial process such as, film blowing, fibre spinning and blow moulding. All these process involves orientation of molecular structure in the flow direction and at high deformation rates (Gupta and Shridhar, 1998). The melt strength can be used as a measure of melt quality. Melt strength is an important property that relates very much of processing characteristics of polymer (Goyal, 1995). For example, bubble stability in film blowing is controlled by melt strength of the polymer. In extrusion coating, higher melt strength leads to lower degree of neck-in (Goyal, 1995). Because of non- homogeneous strain and temperature along the strained strand, it is not considered as well defined property (Dealy and Wissbrun, 1990a). In addition, extensional response is also subject to pre-shearing experienced by polymer in the molten state. Despite all these disadvantages, melt strength is the property that gives the real picture of simultaneous shear and extensional deformation during polymer processing (Micic et al., 1996).

Göttfert Rheotens melt strength tester (Buchen, Germany) (figure 3-7Figure 3-7) is commonly used for uniaxial extensional flow measurement ((Dealy and Wissbrun, 1990b, Muke et al., 2001b)). This equipment is a modification of the Meissner's rotary clamp homogeneous stretching device (Joachim, 1972). The Rheotens serves as useful means for measuring the extensional properties of molten polymers by drawing a vertical strand at a constant acceleration. It measures the force required to extend the polymer strand and the software, Rheotens 97, calculates extensional stress and draw ratios. Pulling speed or acceleration, extrudate mass flow rate, density, etc, are important parameters and all these values are fed into the parameter editor program (PARATens) forming the basis of each test. Calibration is one of the most important issues prior to start any test. Force calibration was done by known weight of 2 N, which is hung on the air-supported wheel. Slow turning of the wheel was maintained by compressed air. Haake single screw extruder was used for the extrusion of the polymer. Detailed information about dimensions of this extruder is discussed in the following table 3-4.

Table 3-4 Specifications for the Haake single screw extruder

Capillary diameter of the extruder	2 mm
Length of the extruder	40 mm
Die entrance angle	120 °
Extruder screw diameter	19.05 mm
Length to diameter ratio	25 mm

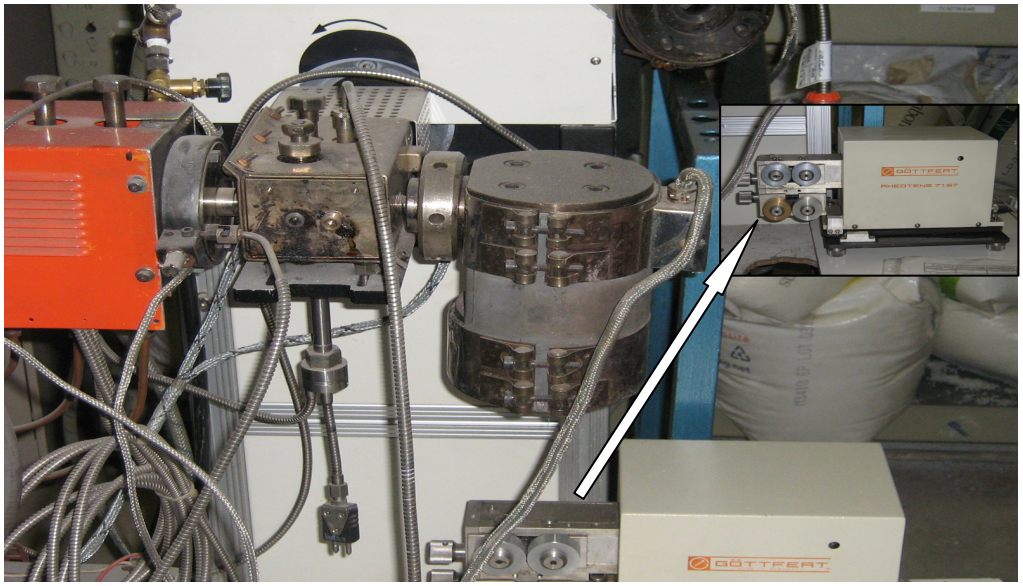


Figure 3-7 Göttfert Rheotens melt strength tester and Haake extruder connected with melt pump.

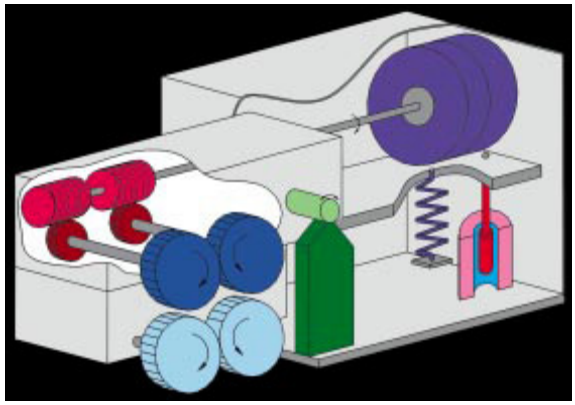


Figure 3-8 Schematic diagram of Rheotens instrument (Goettfert).

The extrusion pressure was read by means of a pressure transducer measured upstream of the die. The extrusion flow rate of 3.9×10^{-3} kg/sec was kept constant by a feed-back loop that controlled the gear pump. Extrusion mass flow rate was measured by means of stop watch and electronic balance. Five repetitions were done followed by average value calculations before and after each run to ensure there were no deviations from the required value. Three temperature controllers were placed to measured and controlled temperatures of different zones at barrel walls. Sufficient time was given before commencement of the run to equilibrate the screw and barrel wall temperature because of placement of temperature controllers on the barrel wall.

The length of the spin line (distance between die exit and entry of Rheotens rollers), $L_{0,}$ was constant and equal to 210mm. The extruded melts were drawn by four counter-rotating wheels of which the top two were mounted on a beam balance (figure 3-8). The bottom rollers served to guide the drawn filament away from the top rollers. The tensile force experienced by the strand was measured and plotted as a function of take-up velocity. Force calibration was conducted before commencing the experiments. Also the initial take-up speed was adjusted such that the drawn force was zero before the start of each run. The velocity of the rollers increased at a constant acceleration of 12 cm/ sec^2 until the extruded strand broke and the force at which this breakage occurred is termed as the "Melt Strength" (Dealy and Wissbrun, 1990b). Due to very high draw rates in this measuring system, inertial and gravitational forces have been neglected (Micic et al., 1996).The temperature at the die was set at 200°C and this was confirmed using a thermocouple. It can be assumed that cooling of the extruded strand in the spin line is small, and the polymer melt is elongated under quasi-isothermal conditions (Wagner et al., 1996). The Rheotens was operated in combination with the PC program EXTENS. This is a real-time data- acquisition program, which displays and stores the measured data of tensile force and drawdown speed.

Extensional viscosity is also one of the important processing parameters. Calculations of transient elongational viscosity in case of isothermal or quasi-isothermal drawing of filament have been described elsewhere (Laun and Schuch, 1989, Prasad et al., 2005). Tensile stress (σ_E), strain rates ($\dot{\varepsilon}$) and extensional viscosity (η_E) calculations were done based on equations 3-6 to 3-9 respectively. These apparent extensional viscosity calculations are considering parameter at the nip roller instead of spin line.

$$\varepsilon = \ln \frac{v}{v_0} \quad \textbf{(3.6)}$$

$$\sigma_E = \frac{F_v}{A_0 v_0} \quad \textbf{(3.7)}$$

$$\dot{\varepsilon} = \frac{v}{L_s} \ln \frac{v}{v_0} \quad \textbf{(3.8)}$$

$$\eta_E = \frac{\sigma_E}{\dot{\varepsilon}} \quad \textbf{(3.9)}$$

Where, v = Velocity of the wheels; v_o = velocity of the extrudate; F = draw force;

Ao= C/s area of the die; Ls = draw distance.

3.2.2. Modulated Differential Scanning Calorimetry (MDSC)

Modulated differential scanning calorimetry is the characterisation technique to determine thermal response of the material. Basically, the instrument consists of two plates, one is reference plate and one is for testing sample. These two pans (A and B in figure 3-9) are individually heated in the presence of nitrogen atmosphere. The difference in heat flow between these two plates will give melting and crystallisation peak. In this method, polymer is heated in the sample pan. Polymer absorbs heat given by heater to melt the polymer before its melting point temperature. After melting point, polymer absorbs heat as a latent heat of melting which is required to convert polymer solid to liquid form and it release the same amount of heat absorbed at crystallisation temperature of the polymer. Figure 3-9 shows the schematic diagram of the equipment assembly.

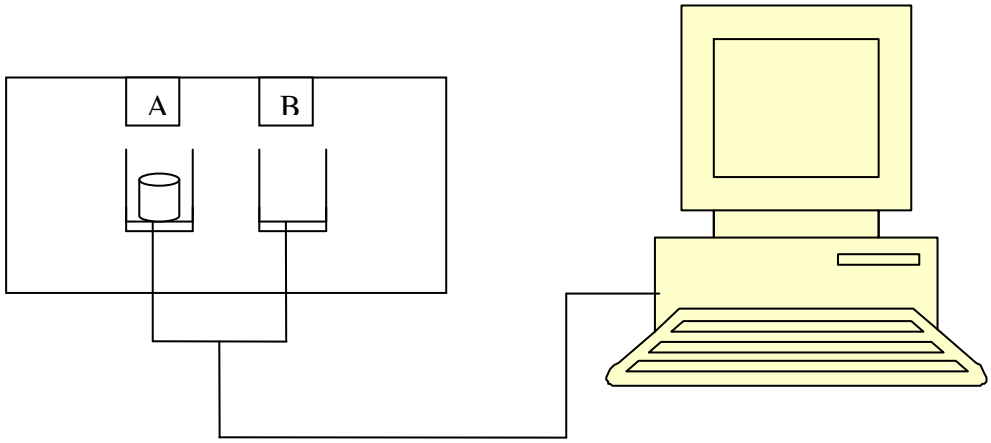


Figure 3-9 Schematic diagram of differential scanning calorimetry

Thermal analysis of the modified and unmodified samples of virgin and post consumer recycled HDPE resin (R-HDPE) were carried out in modulated differential scanning calorimetry (MDSC, DSC 2920 modulated DSC with Thermal Analyst software, TA Instruments, USA) (Figure 3-10). Temperature calibration and cell constant determination of MDSC was done using a known sample (Indium, melting point=156.28 °C and standard heat = 28.42 °C J/g). All the tests were conducted using helium as purge gas (30 ml/min flow rate) and nitrogen as environment gas (100 ml/min flow rate). The heating and cooling rate were constant at 2 °C/min using 0.5 °C modulation amplitude and at a 40-s modulation period. Sample weight was kept between 5-10 mg. The results were analysed in the second heating and cooling curves. The crystallisation temperature (T_c) was recorded. Crystalline melting temperature (T_m) and heat of fusion (ΔH_f) were measured during the second heating cycle. The degree of crystallinity was calculated via the total enthalpy method, according to the equation $X_c = \Delta H_m/\Delta H^+_m$; where X_c is the degree of crystallinity, ΔH_m is the specific enthalpy of melting, and ΔH^+_m is the specific enthalpy of melting for 100% crystalline PE. The ΔH^+_m value for 100% crystalline PE is taken as 288 kJ/kg as reported in the Wunderlich and Czornyj (1977).

Figure 3-10 TA instrument (MDSC-2920) connected with computer software Universal Analysis and Thermal Advantage.

3.2.3. Gel Permeation Chromatography (GPC)

There are various type of relationships exist between rheology and molecular weight properties (Dealy and Wissbrun, 1990b). Relaxation time and MWD are proportional factor; enhancement in MWD results in broad relaxation spectrum and *vis versa*. Gel permeation chromatography (size exclusion chromatography) is the well-known characterisation technique to determine the molecular properties of the polymer. For example, Mn, Mw, degree of branching or branching index (g'), polydispersity index etc.

Polymer samples were prepared in small vials with 1,2, 4-tri-chloro benzene (TCB) as a solvent. Care was taken to ensure the weight of the polymer and the solvent in the vial. Normally, solution of 1,2, 4-tri-chloro benzene and the polymer in the vial is loaded into the GPC equipment. After that the solution of polymer is pumped down a column which is packed with a porous material. Molecules of the polymer diffuse through the porous material but small molecules trapped into the pores of the packing material and big molecules easily reach the end of the column. Small molecules have to travel lot more than big molecules to reach at the end of the column. The time taken by different size of molecules is converted to molecular weight. Calibration was performed by the polymers having known MWD before the experimental run of the samples.

GPC analysis was performed at 140 °C using Waters Alliance GPCV2000 equipment (figure 3-11).This equipment consists of differential refractive index (DRI) and viscometer detectors. 1, 2, 4-tri-chloro benzene (TCB) was used as a solvent, with a flow rate of 1.00 ml/min. Chromatograms were analysed using the Millennium® software.

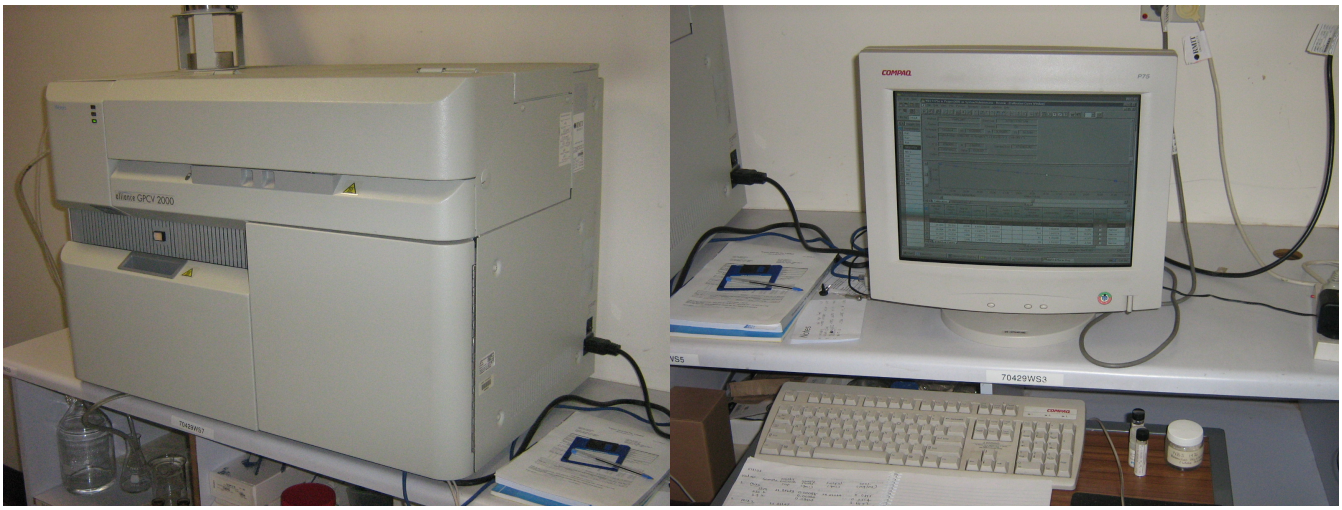


Figure 3-11 Gel Permeation Chromatography (GPC) equipped with Millennium® software

3.2.4. Mechanical Characterisation

Determination of tensile properties was carried out according to ASTM standards D 638-01 (ASTM D638-01, 2001) using the Instron Universal Testing Machine (model no. – 4467. Instron Corporation, England). Schematic diagram of tensile testing equipment is shown in figure 3.12. Load calibration was done prior to the test. Gauge length was adjusted according to the degree of elongation. Plaques (2 mm thick) of the samples were compression moulded at 190°C and 120 kN (27,000 lbs) for 5 minutes, followed by cooling to 50°C within 7 minutes@ cooling rate of 20-30° C/min according to the requirements of ASTM D638-01 (ASTM D638-01, 2001) for tensile testing. Specimens were cut into dumbbell-shape (type I), these plaques were conditioned for at least 40 hours at 23° C $\pm$ 2° C and 50% $\pm$ 5% relative humidity prior to testing on an Instron Universal Testing Machine at 50mm/min crosshead speed. An average thickness and length were measured three times using digital Vernier scale and averaged values were inserted into the Instron software. Test specimens were fitted carefully into the gap between grips at upper and lower sides as shown in figure 3-12.

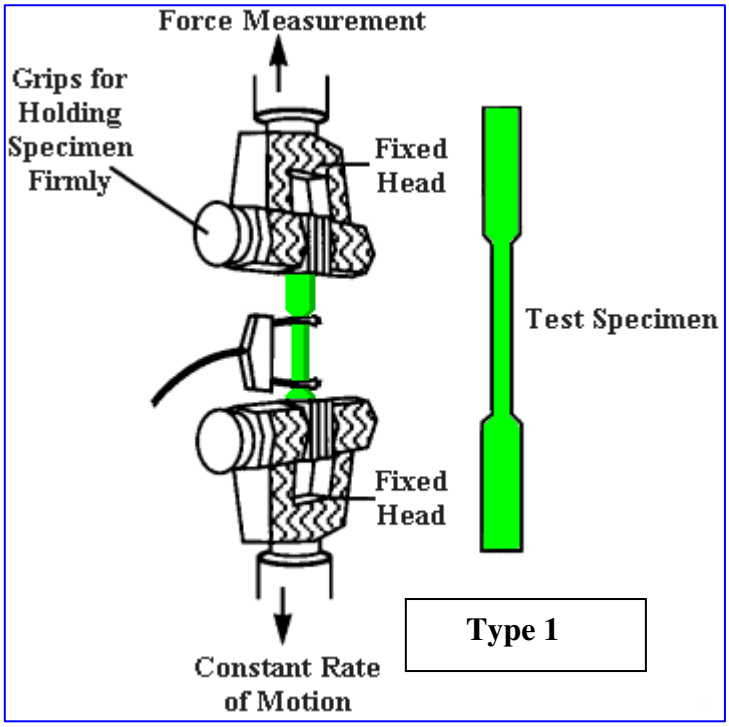


Figure 3-12 Schematic Diagram of Instron Tensile Testing Machine
(http://www.matweb.com)

For each sample (in terms of peroxide concentration, refer table 3-3), 5 specimens were used for both Young's modulus and tensile strength properties. The main objective of this test is to have a comparative insight into the mechanical behavior of the investigated samples. Stress-strain curves were recorded using following equations for the calculation of stress (σ) and strain (ε):

$$\sigma = \frac{F}{A_0} \qquad \textbf{(3.10)}$$

Where F is the applied force in N and A_0 is the cross-sectional area of the sample in mm^2.

$$\varepsilon = \frac{(L - L_0)}{L_0} * 100 = \frac{\Delta L}{L_0} * 100\% \qquad \textbf{(3.11)}$$

Where ΔL is the change in the gauge length of the specimen relative to the initial sample length L_0

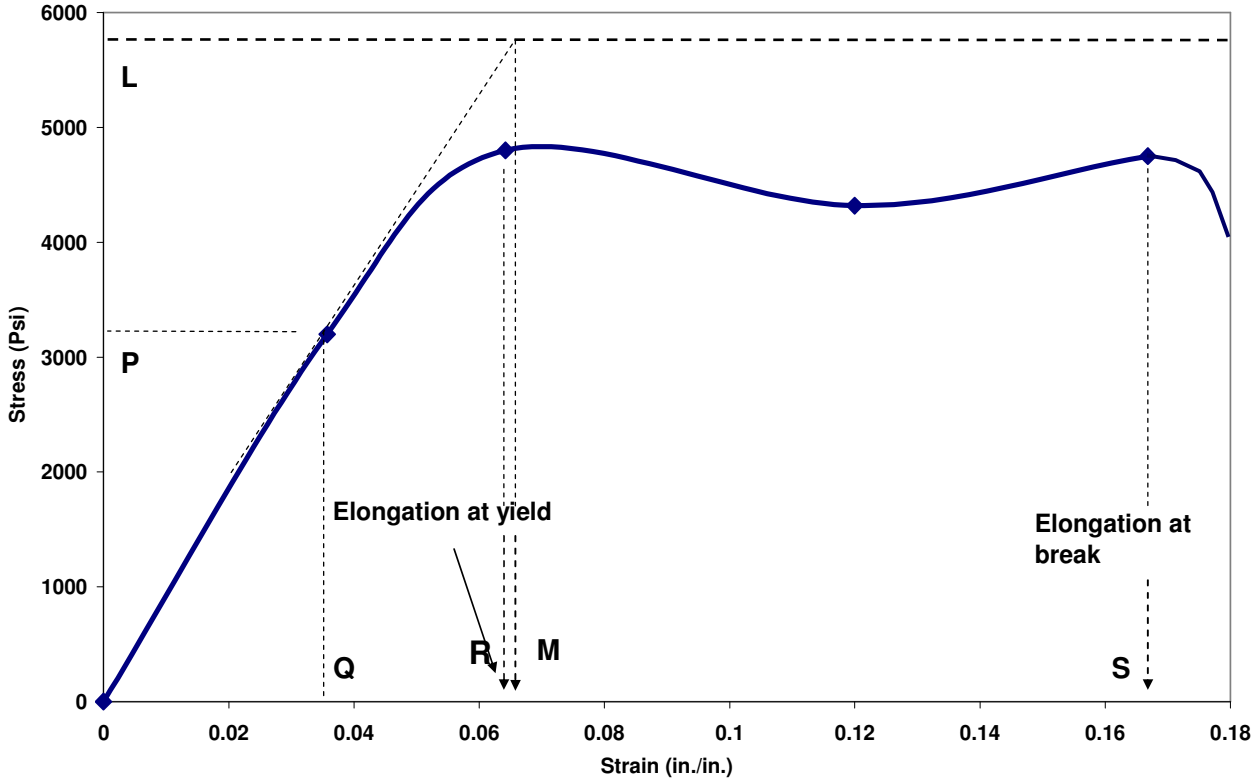


Figure 3-13 Tensile test curve (Stress-Strain Curve)
(http://aemes.mae.ufl.edu/~uhk/strength.htm)

The modulus of elasticity (Young's modulus) was determined by the slope of the initial part of the stress-strain curves (figure 3-13).

$$Young's Modulus = \frac{L - P}{M - Q} \quad \textbf{(3.12)}$$

Tensile strength at yield σ_y is the stress at which the sample yields, divided by its cross-sectional area:

$$\sigma_y = \frac{F_y}{A_0} \quad \textbf{(3.13)}$$

Where F_y is the applied force at yield in N and A_0 is the initial cross sectional area of the sample in mm^2.

3.2.5. Bent strip test for Environment Stress Cracking Resistant (ESCR)

The bent strip was originally designed at Bell laboratories for assessing the properties of wire cable coatings. It has been widely accepted as a common laboratory method for assessing ESCR of polymeric materials. Notched specimens, a strong surfactant and constant high temperature were used to speed up the effects of environmental conditions the polymers would encounter in service.

Plaques (2 mm thick) of the samples were compression moulded at 190°C and 120 kN (27,000 lbs) for 5 minutes, followed by cooling to 50 °C within 7 minutes@ cooling rate of 20-30 °C/min according to the requirements of ASTM D1693-01 (ASTM D1693-01, 2001) for ESCR testing. Specimens were cut from these plaques and conditioned for at lease 40 hours at 23 °C $\pm$ 2°C and 50% relative humidity prior to testing. Ten specimens of each sample were notched. Placed in the specimen holders and immersed in a surfactant solution of 10 vol% Igepal CO-630 (figure 3-15) at 50 °C. The specimens were checked at intervals manually and the time for at least five of the ten specimens to fail, f_{50} was recorded. Routine inspection was done every 2 hours after the first crack growth was observed in the sample. For example, ten specimens of virgin HDPE was put in testing condition and at regular interval it was observed for initial crack growth and further growth in this crack. When initial crack and further growth in this crack was observed for any five specimens out of ten then this reading was taken into account for particular sample. Equipment set up is shown in figure 3-14.

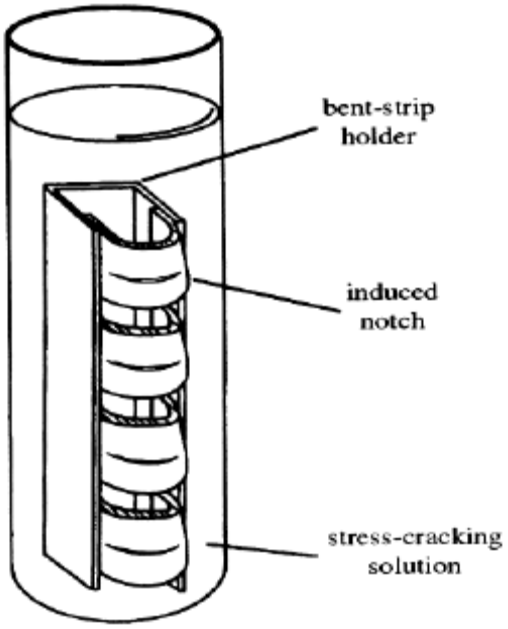


Figure 3-14 ESCR equipment setup
(Andersen, 2004)

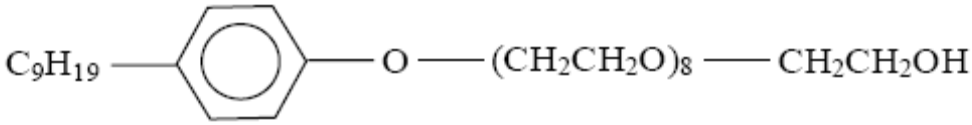


Figure 3-15 Chemical formula of Igepal CO-630
(Andersen, 2004)

3.3. ERROR ANALYSIS

Previous section described experimental procedures, equipment operations and materials used in this work. In the most of the cases, some inherent errors may arise from experimental measurements. It is very important to discuss these errors briefly.

3.3.1. Shear Rheological Measurements

Dynamic strain sweeps and frequency strain sweeps were performed as a part of oscillatory shear measurements. Four important aspects of oscillatory shear that need to be discussed are

- Temperature accuracy of the ARES rheometer during the test runs.

According to the manufacture's specification, temperature accuracy of the ARES rheometer is $\pm$ 0.1 °C and torque range is 0.0 g_f-cm to 2000 g_f-cm. Time sweep was performed to test the temperature accuracy of the ARES rheometer. According to the time sweep test (figure 3-16), temperature accuracy was approximately the same as manufacturer's specifications.

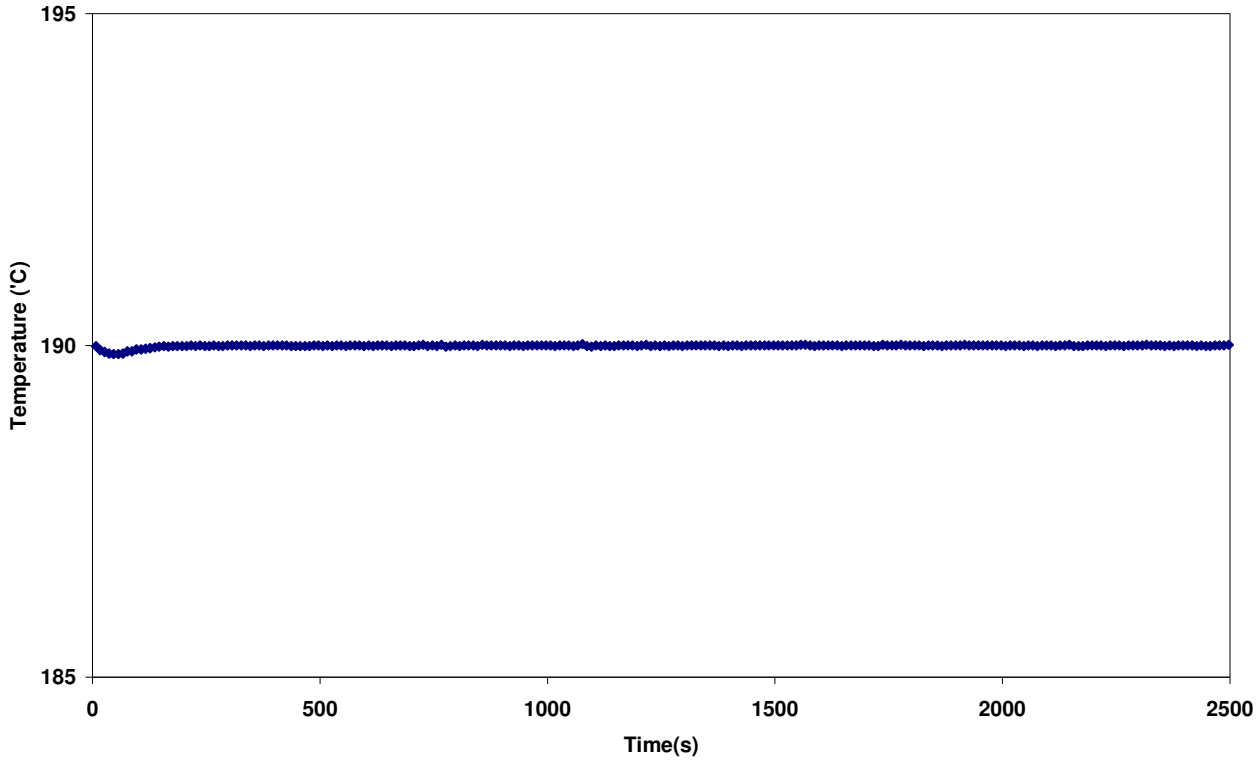


Figure 3-16 Temperature sensitivity of the ARES rheometer for long time range. Deviation of $\pm$ 0.01 °C was observed for unmodified V-HDPE at 0.1 rad/s.

- Repeatability or reproducibility of the runs to make sure consistency of the measurements.
- Stability of the measurements; particularly at low frequencies (0.01 rad/s to 0.001 rad/s).

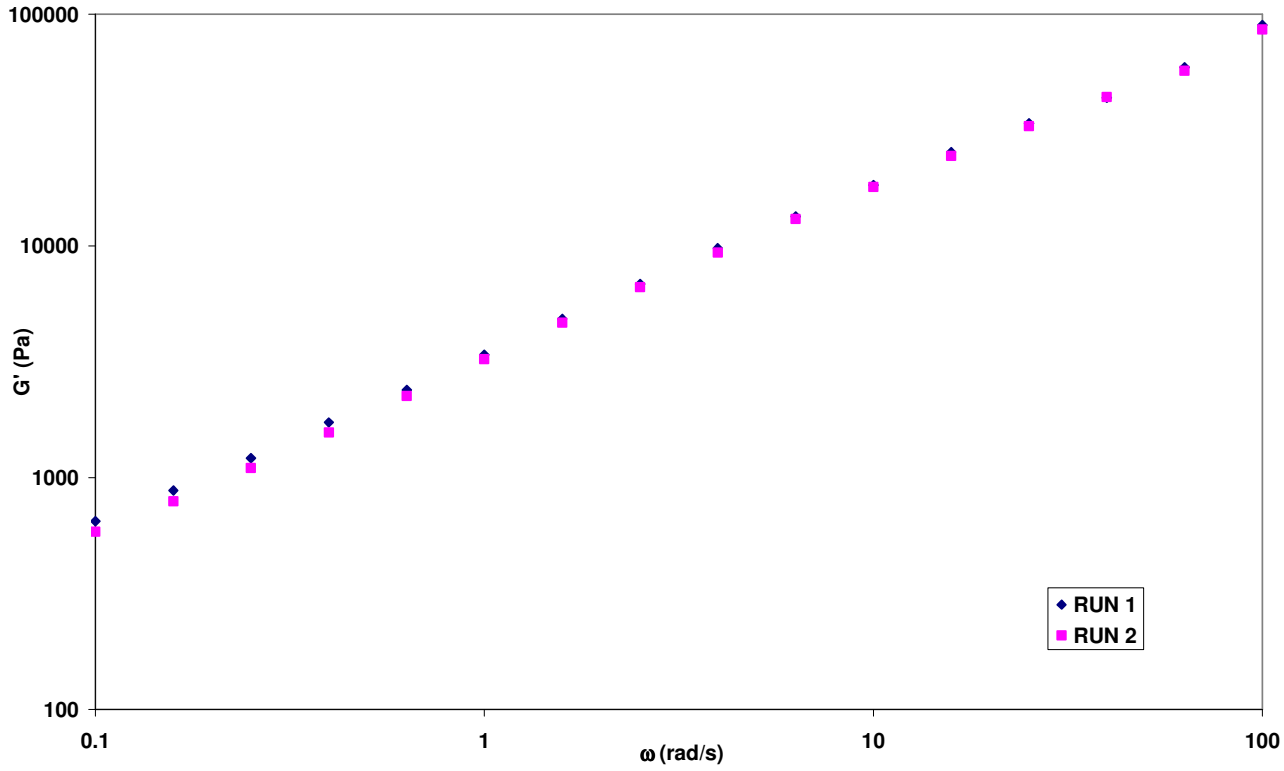


Figure 3-17 Repeatability of V-HDPE (0.1 wt% DCP) samples using dynamic frequency sweep at 190 °C

Figure 3-17 shows repeatability of dynamic frequency experiments conducted for V-HDPE modified by 0.1 wt % DCP at 190 °C. Repeatability of these runs was excellent for intermediate and high frequencies as both data points were overlapping. In the low frequency region, it seems to be slightly deviated and this could be due to the approach of torque-strain relationship to the limit of instrument sensitivity. This behaviour has been observed for all samples tested at low frequency region. An average of two runs were chosen and presented in the results and discussion chapter of the thesis to minimise the error occurred during dynamic frequency tests.

- Thermal degradation of the virgin and recycled HDPE samples with and without peroxide modification at elevated temperature for long time ranges.

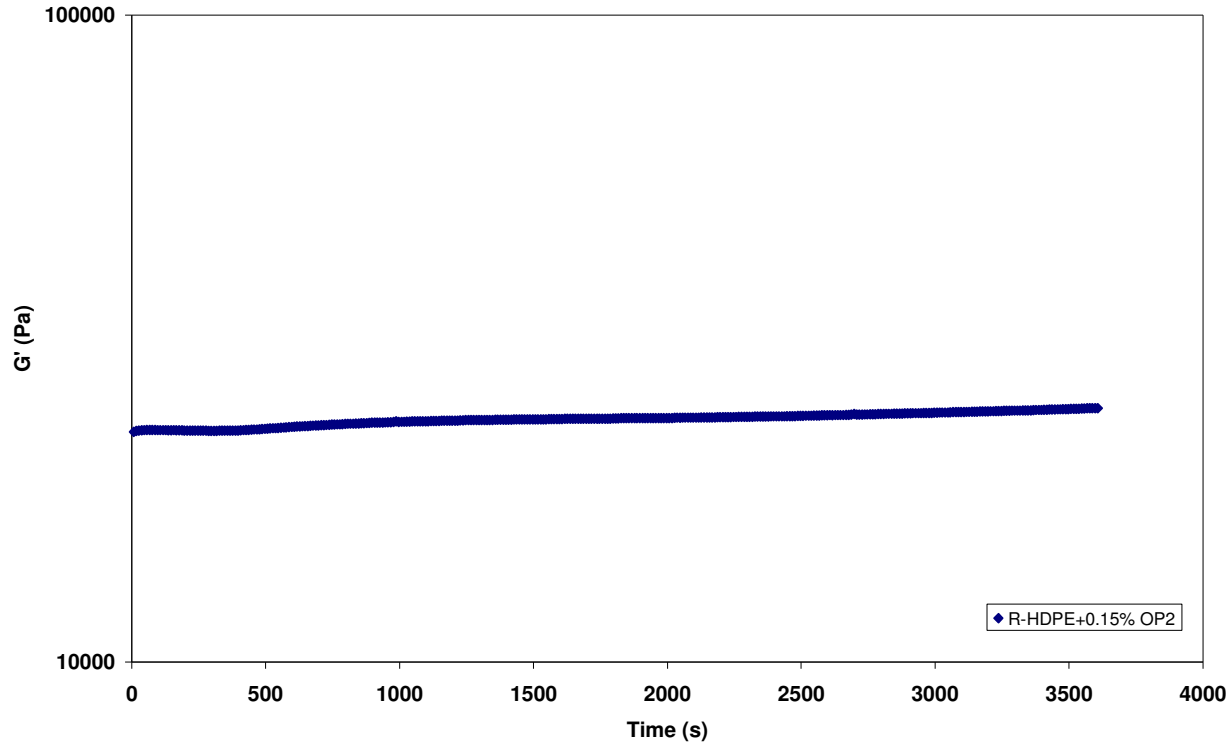


Figure 3-18 Dynamic time sweep for R-HDPE + 0.15 wt% OP2 sample to check for thermal degradation of sample (ω=0.1 rad/s)

Dynamic frequency sweep tests were performed for all sample and these all tests were performed over wide range of frequencies and hence for a long period of time. Some time it is very difficult to avoid thermal degradation of the sample at very high temperatures although nitrogen atmosphere was provided to avoid thermal degradation of the sample. Thermal degradation of the samples subjected to elevated temperatures for long time can have adverse effect on their microstructure. Changes in microstructure can lead to chain scission and cross-linking and/or other physico-chemical process that can adversely affects the material properties. Dealy and Wissbrun (1999) suggested that, thermal degradation of the sample can be measured by using dynamic measurement. A frequency of 0.01 rad/s was chosen as this frequency is in the range of low frequencies and it took long time for the sample to approach this frequency. Also recycled HDPE modified by OP2 with highest wt% (0.15%) was chosen for dynamic time sweep as highest peroxide level in the recycled HDPE has higher risk of thermal degradation. Time length of the time sweep was selected corresponding to the longest run when dynamic frequency sweep measurements were conducted. Temperature of 190°C was selected which is same temperature used for dynamic frequency sweeps. Figure 3-18 shows the dynamic time sweeps for R-HDPE + 0.15% OP2. It can be seen from the

figure that, G' (most sensitive to changes in the microstructure) remained unchanged over a long period of time and thus no thermal degradation was observed.

3.3.2. Melt Strength test (Göttfert Rheotens melt strength tester)

The Rheotens test involves continuous drawing of a monofilament through two counter-rotating wheels. The output of the test is a force versus draw ratio plot. Melt strength test is not well-defined rheological properties as mentioned previously. This is due to the non-isothermal and non-constant strain rate of the filament during the test. It is very difficult to measure the local temperature of the drawn filament and also test was not carried out at constant velocity. These tests were carried out at constant acceleration of 12 mm/s^2. Aspects which are considered in these set of experiments were:

- Effect of cooling. It was observed that, during the initial slow velocity, the drawn filament would be expected to cool at a faster rate but at high rates, the extent of cooling of the filament minimized and the stretching can be pseudo isothermal.

- Muke et al (2001c) have shown that increasing flow rate has an exponential effect on melt strength. That is why it is very important to maintain the same mass flow rate throughout each run. Prior to each run, three extrudate flow rates were taken and averaged to overcome the error. The mass flow rates were all within $\pm$ 1% of the desired value of 3.9 g/min.

- The precision of the Rheotens data were checked using repeatability analysis. Each virgin and recycled HDPE sample was run 10 times and from that best 5 curves were selected to take melt strength as the average value at the plateau or in the draw resonance region of the force-draw ratio plots. Figures 3-19 and 3-20 show melt extensional profiles of unmodified V-HDPE and V-HDPE + 0.15% DCP respectively. In both cases, higher error can be observed at low draw ratio region than higher draw ratio region. This could be due to the solidification of the drawn filament during the low draw ratio. At high draw ration cooling extent minimized and hence higher precision at higher draw ratio prior to draw resonance or any instability.

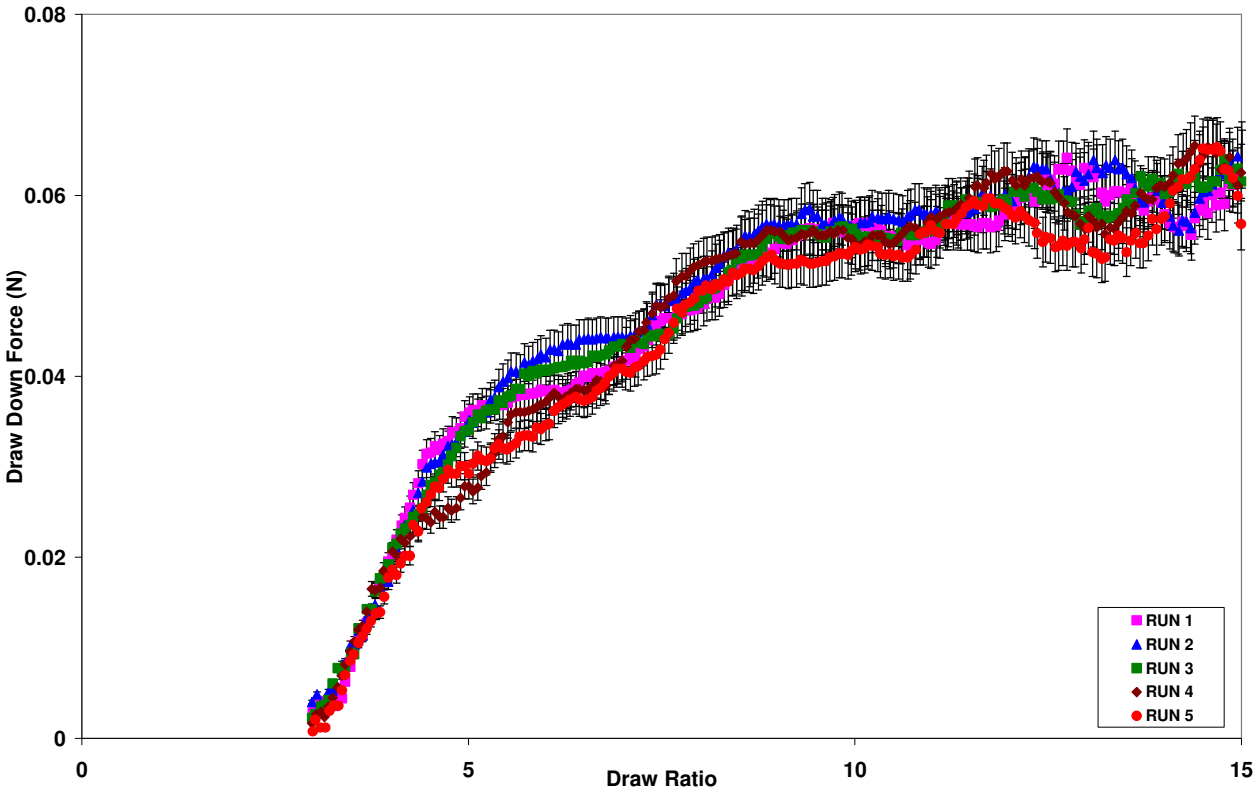


Figure 3-19 Repeatability tests for V-HDPE at 190 °C and 12mm/s^2 of nip roller acceleration

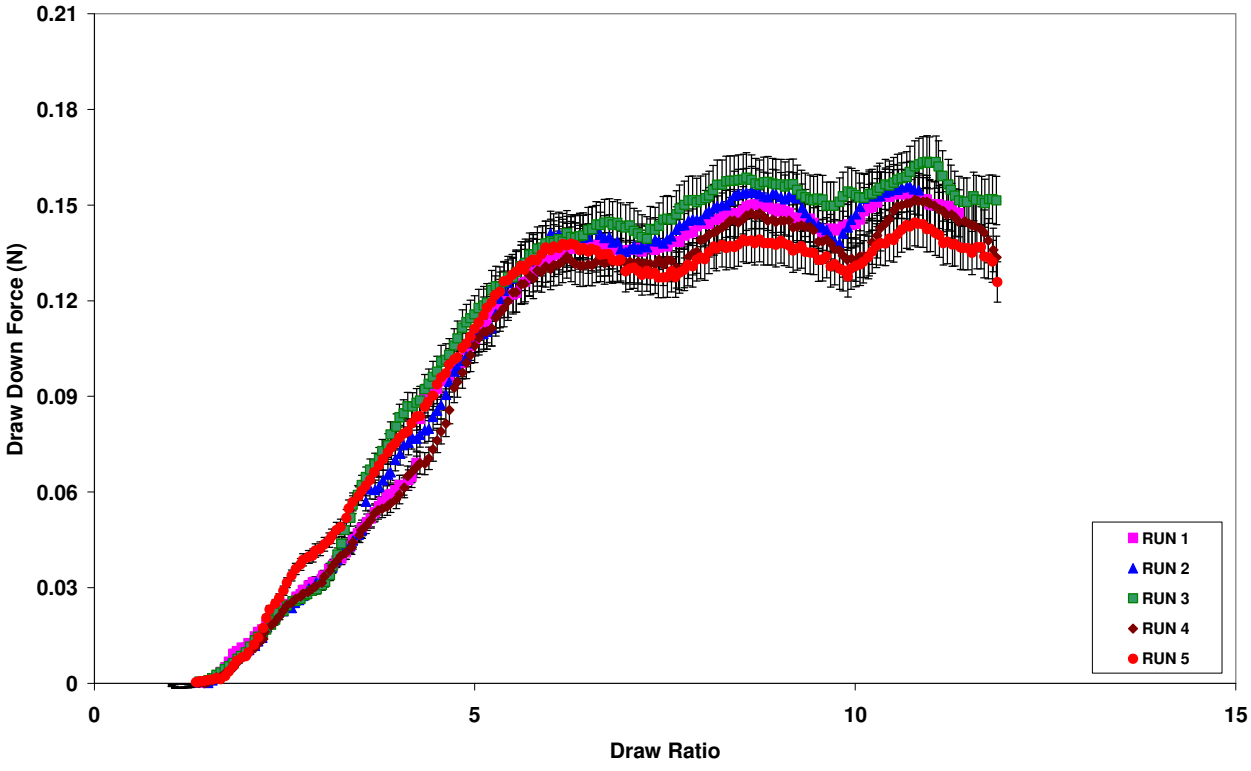


Figure 3-20 Repeatability tests for V-HDPE + 0.15% DCP at 190 °C and 12mm/s^2 of nip roller acceleration

CHAPTER 4. RESULTS AND DISCUSSION

This chapter will present and discuss the results of experimental work performed on the unmodified and modified virgin and recycled HDPE. In addition, detailed discussion on analysis of results obtained will be provided for better understanding of the reactive extrusion process and its implications on various enhanced properties. The experiments and relative analysis that were carried out are outlined below:

- Flow and processability of the modified materials' under shear and extensional deformations.
- Thermal transition of the modified materials within the processing temperature range.
- Effects of peroxide modification on the molecular structure and hence final materials' properties.
- Tensile behaviour of the modified materials.
- Performance of the modified materials under the environmental stress.

Rheological analysis will be discussed as below which is based on the experiments performed.

- Shear rheology
    - Dynamic shear rheology
        - Dynamic strain sweep (linear viscoelastic region determination)
        - Dynamic frequency sweep (small amplitude oscillatory shear)
- Uniaxial melt extensional measurement (melt strength)

4.1 *SHEAR RHEOLOGY*

The viscoelastic properties of organic peroxide treated V-HDPE and R-HDPE resins were measured by advanced rheometric expansion system (ARES), equipped with parallel plate geometry. Deformation and the flow of the material are very important when it is tested under the influence of applied stress. It is important to note that, the measurements were performed within the linear viscoelastic region (10% strain) as viscoelastic properties are dominated by chain structure within linear viscoelastic

region. The viscoelastic shear properties of the polymers were studied by measuring the storage modulus (G'), loss modulus *(G")* and the complex viscosity (η*) within the linear viscoelastic region of the polymers. The storage modulus measures the elastic response of a polymer while the loss modulus measures the viscous energy dissipated during flow deformation.

4.1.1 Linear Viscoelastic Region

Before caring out detailed dynamic measurements to probe the sample's microstructure, the linear viscoelastic region (LVER) must first be defined. This is determined by performing an amplitude sweep. The moduli initially are independent of stress, giving a plateau known as the linear viscoelastic region (LVER). Linear viscoelastic region refers to the region in which the internal structure of the polymer would not be affected by shear forces; storage modulus (G'), loss modulus (G") and complex viscosity (η*) is independent of imposed strain within this region. From the amplitude sweep test, stress or strain must be selected from the LVER and incorporated into subsequent oscillation measurements. All these tests are performed at 190 °C and a constant frequency of 10 rad/s.

Figures A-1 to A-4 (appendix) show dynamic strain sweep results for V-HDPE and R-HDPE with five different compositions of DCP and OP2. The plateau region, where storage modulus is independent of strain amplitude, refers to the linear viscoelastic region of these materials. G' is the parameter which is most sensitive to changes in micro structure (Krishnamoorti et al., 2001). These elastic responses experienced initial instability due to instrumental sensitivity limit for strain-torque relationship. Storage modulus is constant with strain amplitude (LVER) after some initial instability for all compositions of organic peroxides with V-HDPE and R-HDPE. However, it can be shown that the magnitude of G' increased with peroxide loading in the low shear rate region. It is due to the larger level of intermolecular interaction between polymer chains (entanglements) by organic peroxide free radical reaction (Couch and Binding, 2000).

Critical strain (γ_c) refers to limit of linearity in the strain sweep measurement. Imposed strain in linear viscoelastic region was not enough to cause any deformation in equilibrium state of the polymer. Moreover, storage modulus was independent of strain amplitude during the quiescent state of the polymer. However, beyond critical strain amplitude (γ_c), it started to deviate monotonically from its LVER value with increase in

strain amplitude. This type of behaviour is most noticeable in polymer solutions and melts. The origin of strain thinning at critical value of the strain (γ_c) is believed to be region similar to that of shear thinning (Hyun et al., 2002). Shear thinning is the most common rheological similarity between diverse complex systems including polymer melts, suspensions, solutions, etc. Chain orientation or alignment of microstructure with flow direction leads to shear thinning and hence deteriorating local drag. In the lower strain region, G' and G" are constant in the entangled state of the polymer. As the strain was increased, disentanglement of the polymer chains results in the alignment of all the chains in the direction of flow. Anisotropic systems represent significant effects of this disentanglement and further reduction in the moduli. The critical strain amplitude (γ_c) point is the origin of nonlinearity for the given polymer (Hyun et al., 2002). Figure 4-1 shows the limit of non-linearity in terms of critical strain amplitude. Generally it can be observed that as the peroxide concentration increased the linear viscoelastic region tended towards lower strain amplitude.

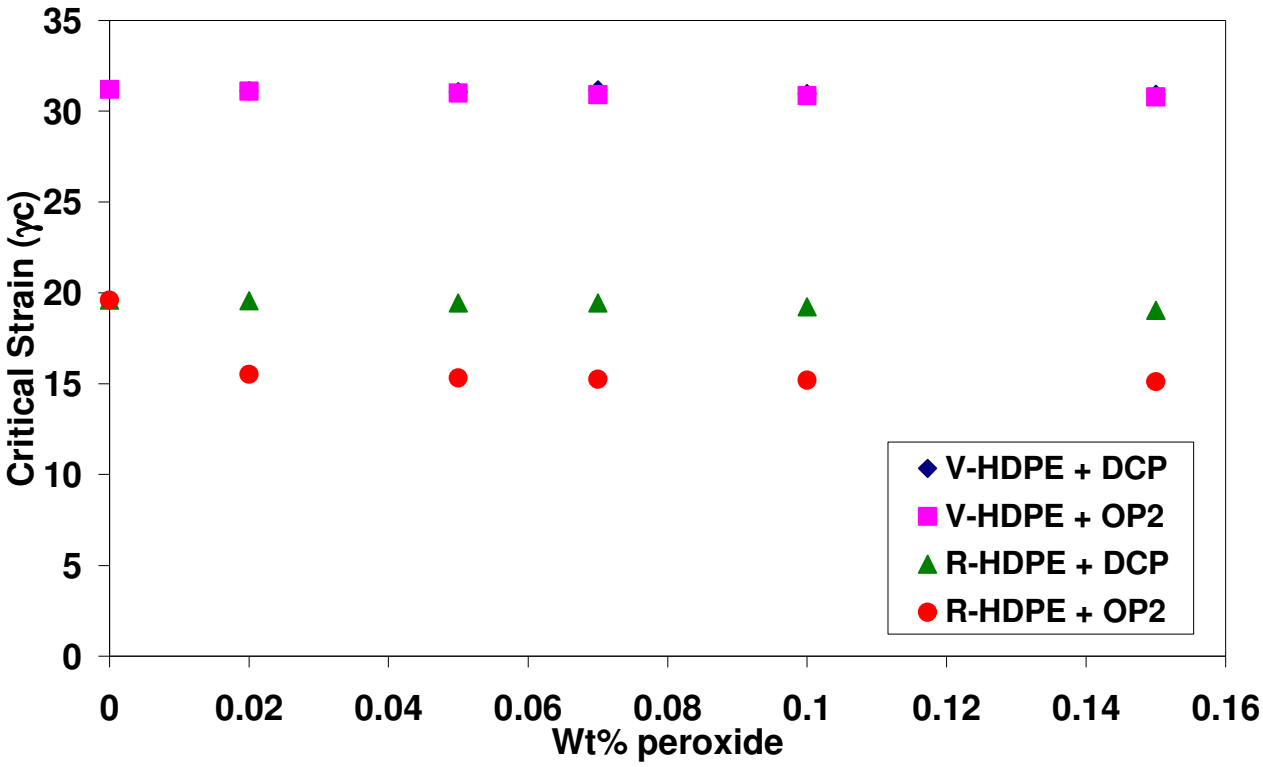


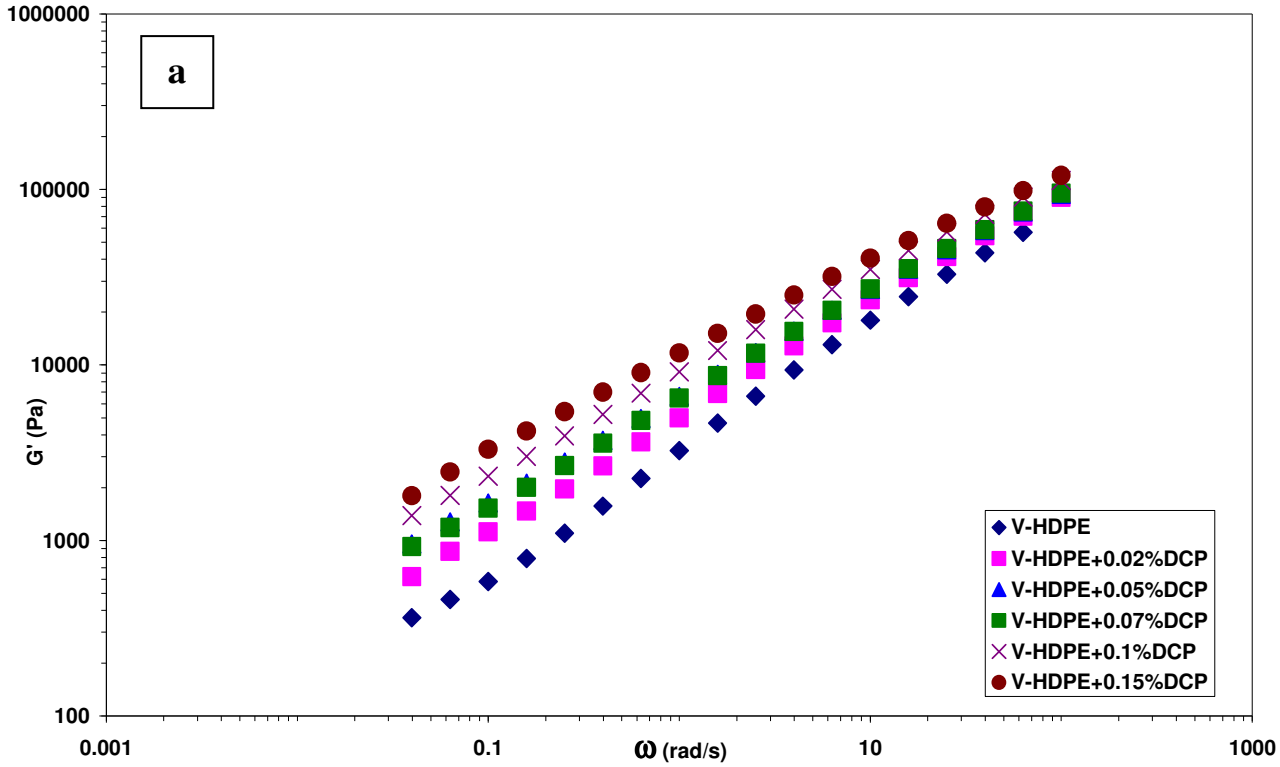
Figure 4-1 Critical strain amplitude (γ_c) as a function of wt% of peroxide for V-HDPE and R-HDPE with both peroxides

4.1.2 Small amplitude oscillatory shear (SAOS)

Extensive study has been undertaken on extended chain mechanism or crosslinking effects on rheology of polyolefins by introducing organic peroxide free radial mechanism (Read and McLeish, 2001, Shroff and Mavridis, 1999, Kim and Kim, 1993b, Bersted, 1985, Tang et al., 1989, Ghosh et al., 1997, Lem and Han, 1982, Kulichikhin et al., 2004, Perez et al., 2002). All of the above works concluded that the organic peroxide crosslinking with polyolefins has significant effect on shear and extensional rheological properties and thus processability of these materials.

Figures 4-2 to 4-5 **Error! Reference source not found.**show frequency dependency of G' (figures 4-2 to 4-5; (a)) and G" (figures 4-2 to 4-5; (b)) for V-HDPE and R-HDPE modified by DCP and OP2 respectively. From figure 4-2 (a) and (b), it can be seen that the storage and loss modulus increased with DCP composition. For composition of 0 wt%, 0.02 wt%, 0.05 wt%, 0.07 wt% of DCP, increase in both moduli are approximately identical. Further, G' dominated over G" at all higher frequencies tested. G' domination at higher frequencies was also observed by Harrell and Nakajima (1984) for frequency dependent viscoelastic properties of the long chain branched polymers. At lower frequencies, G" dominated over G' due to the presence of terminal flow behaviour of liner chains for virgin material as well as all materials modified by lower concentrations of peroxide. For virgin material (0 wt%), values of G' was much lower but it increased significantly after even 0.02 wt% of DCP at lower frequencies and after that a linear increase was observed as DCP concentration increased further. Examination of the low frequency region demonstrates that the contribution of the G' to the total response increases as degree of branching increases. More clearly, enhancement in the branching mechanism provides long time relaxation mechanism therefore enlargement of relaxation spectrum. However, G' curve of virgin HDPE overlapped the other G' curves at higher frequencies. Frequency dependence of storage (G') and loss modulus (G") for V-HDPE modified by OP2 are shown in figure 4-3 (a) and (b) respectively. It can be seen that both the G' and G" enhanced with OP2 loading. Moreover, significant enhancement of both moduli was observed in the low frequency region than enhancement observed in the high frequency region. Formation of branching mechanism is the possible reason for enhancement of G' at lower frequency (Wang et al., 1996). Generally, branching mechanisms have more linkage points and exhibit 3-dimensional network which needs more time to relax as compare to linear

polymer. Thus the effect of branching is more prominent in the lower frequency region. Some researchers worked on star (Raju et al., 1979) branched and randomly branched (Wild et al., 1976) polymers also observed enhancements in G' at lower frequencies. On the other hand, linear increase in G" was noted for all the compositions of OP2 at both higher and lower frequencies, showing that unlike the elasticity, viscous deformation was not much affected by the presence of the crosslink's.



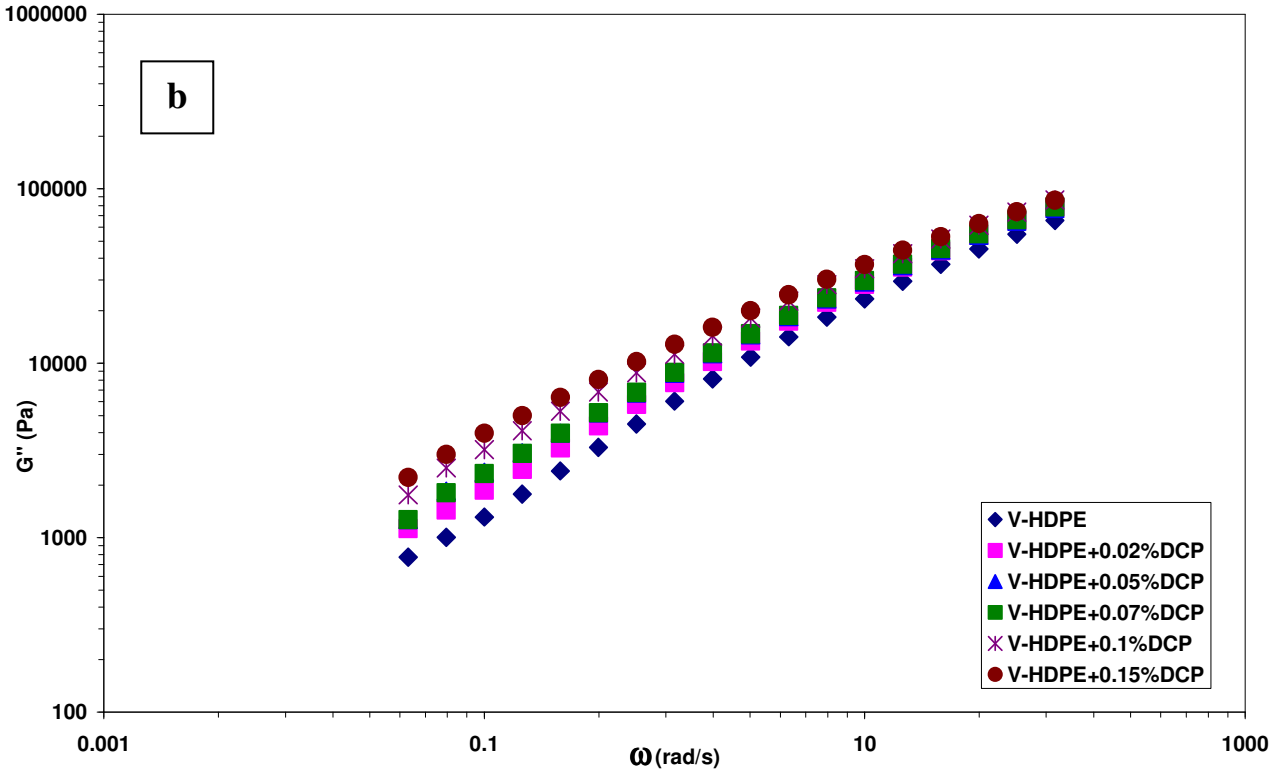


Figure 4-2 Dynamic frequency sweep results for V-HDPE modified by DCP (a) storage modulus (G') (b) Loss modulus (G")

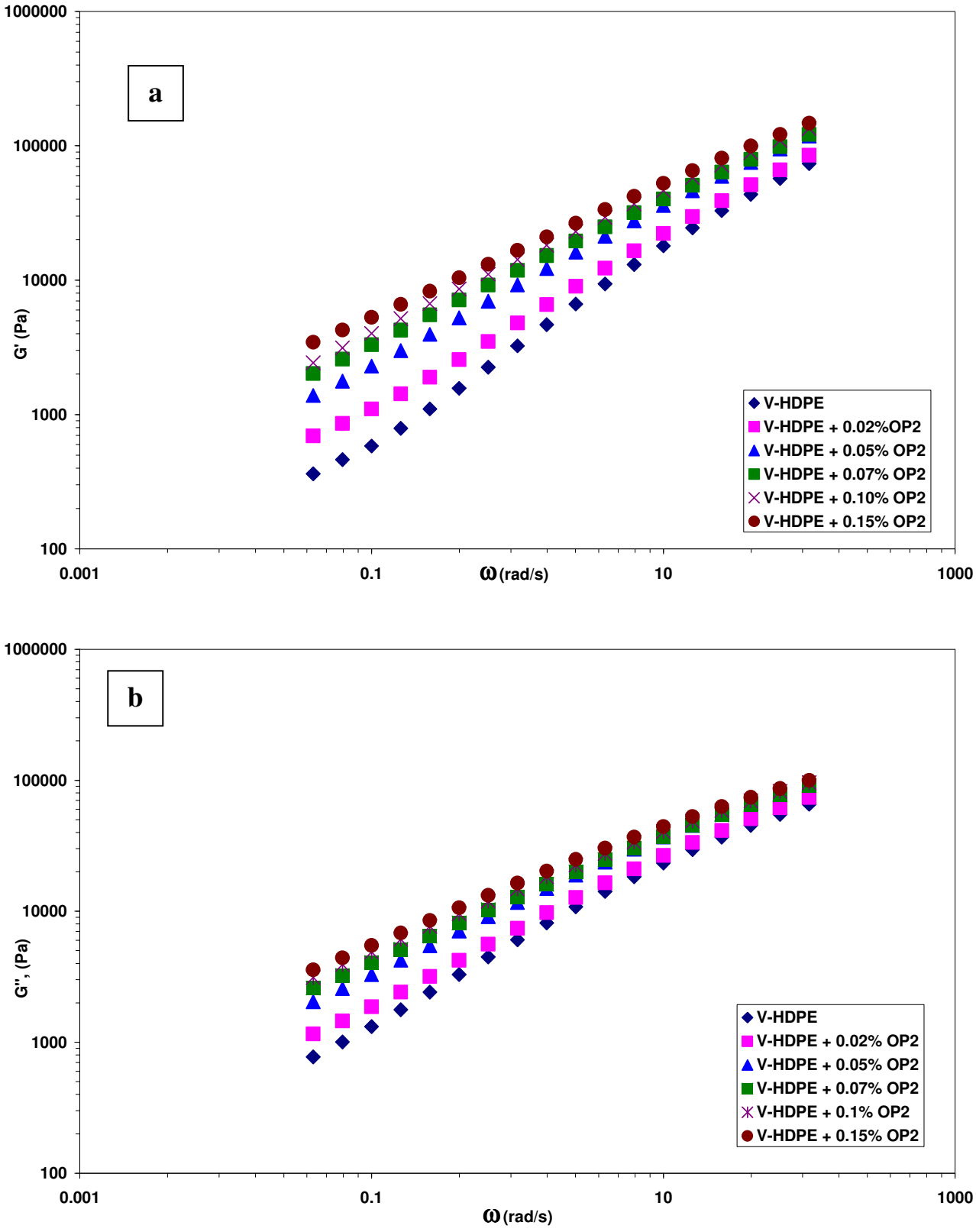
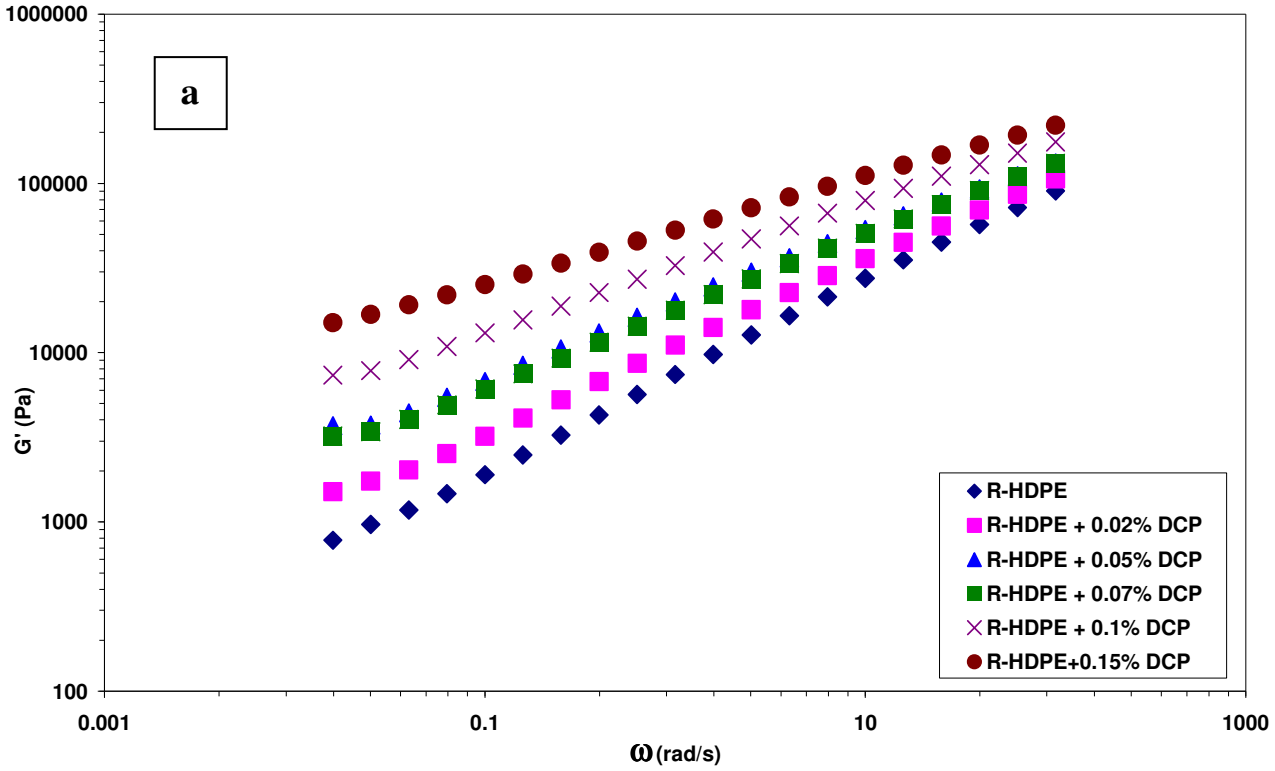


Figure 4-3 Dynamic frequency sweep results for V-HDPE modified by OP2 (a) storage modulus (G') (b) Loss modulus (G")

Figures 4-4 and figure 4-5**Error! Reference source not found.Error! Reference source not found.** show the storage moduli (G') and loss moduli (G") for R-HDPE with DCP and OP2. As shown in figure 4-4**Error! Reference source not found.** (a) and (b), G' and G" both increased with DCP loading in agreement with the observations of other authors (Lem and Han, 1982, Kim and Kim, 1993b, Harlin and Heino, 1995, Ghosh et al., 1997). Frequency dependence of both storage (G') and loss (G") moduli was more pronounced at lower frequencies than at higher frequencies. Both moduli were close to each other at lower concentrations of DCP but at higher concentration (0.10 wt% and 0.15 wt%), G' found to be more sensitive over G" for both frequencies. Composition contained 0 wt% DCP showed the same trend as with virgin material as shown in the figures 4-2 and figure 4-3. Storage and loss modulus for R-HDPE also increased progressively with 1, 3 1, 4 Bis (tert- butylperoxyisopropyl) Benzene (OP2) loading (figure 4-5**Error! Reference source not found.**). Moreover, compositions above 0.02 wt% of peroxide have higher values of both moduli than R-HDPE modified by dicumyl peroxide (DCP) at low frequencies. However, G' and G" overlapped each other at higher frequencies. This overlapping can be attributed to the alignment of branched molecules in the direction of flow due to the higher imposed strain at high frequencies (Hyun et al., 2002). Overall, the strong viscoelastic improvement has been observed with these virgin and recycled grades of high density polyethylene modified by both organic peroxides. These improvements are the result of the formation of larger macromolecules caused by the chain linking reactions (Perez et al., 2002).

It has been observed that long chain branches get aligned in the direction of flow at higher frequencies. Due to this alignment, less contribution was obtained from both the moduli. At low frequencies, imposed strain was not high enough to disturb the meso-structure. Therefore, G' and G" at low and intermediate frequencies were different from those of unmodified HDPE.



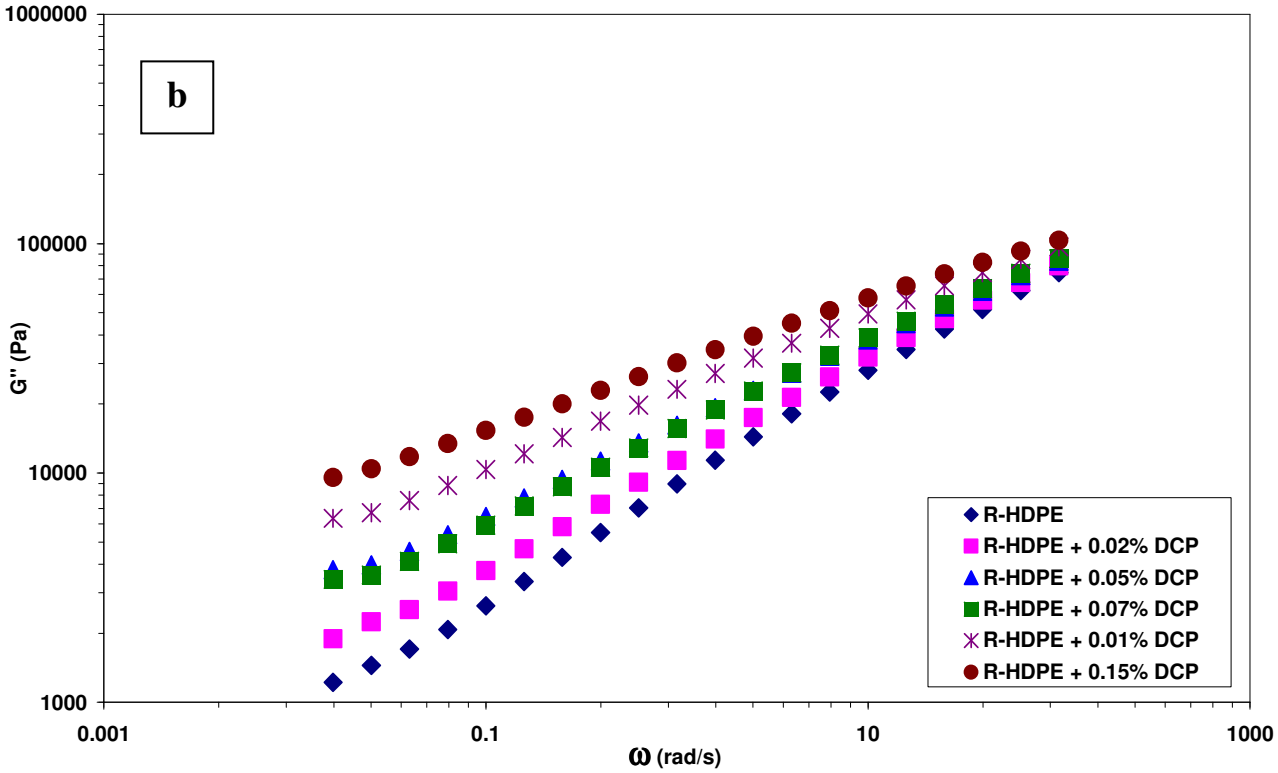
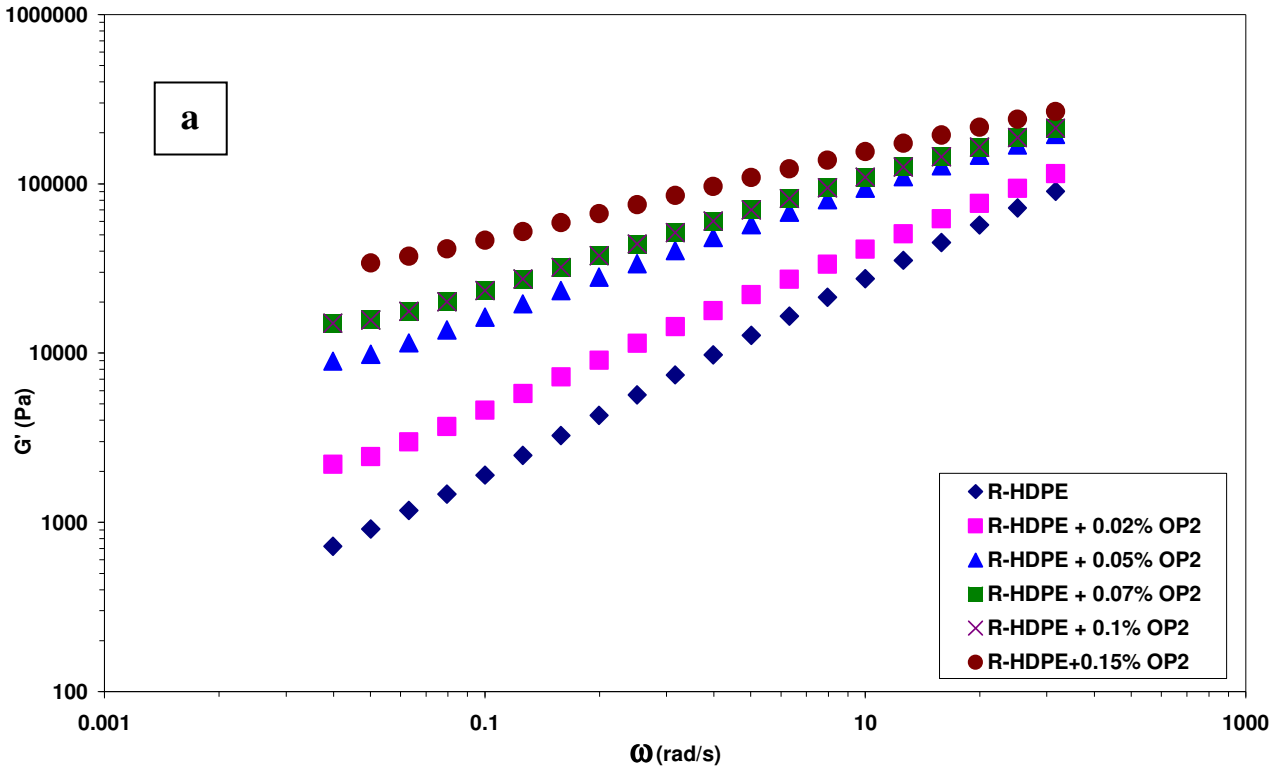


Figure 4-4 Dynamic frequency sweep results for R-HDPE modified by DCP (a) storage modulus (G') (b) Loss modulus (G")



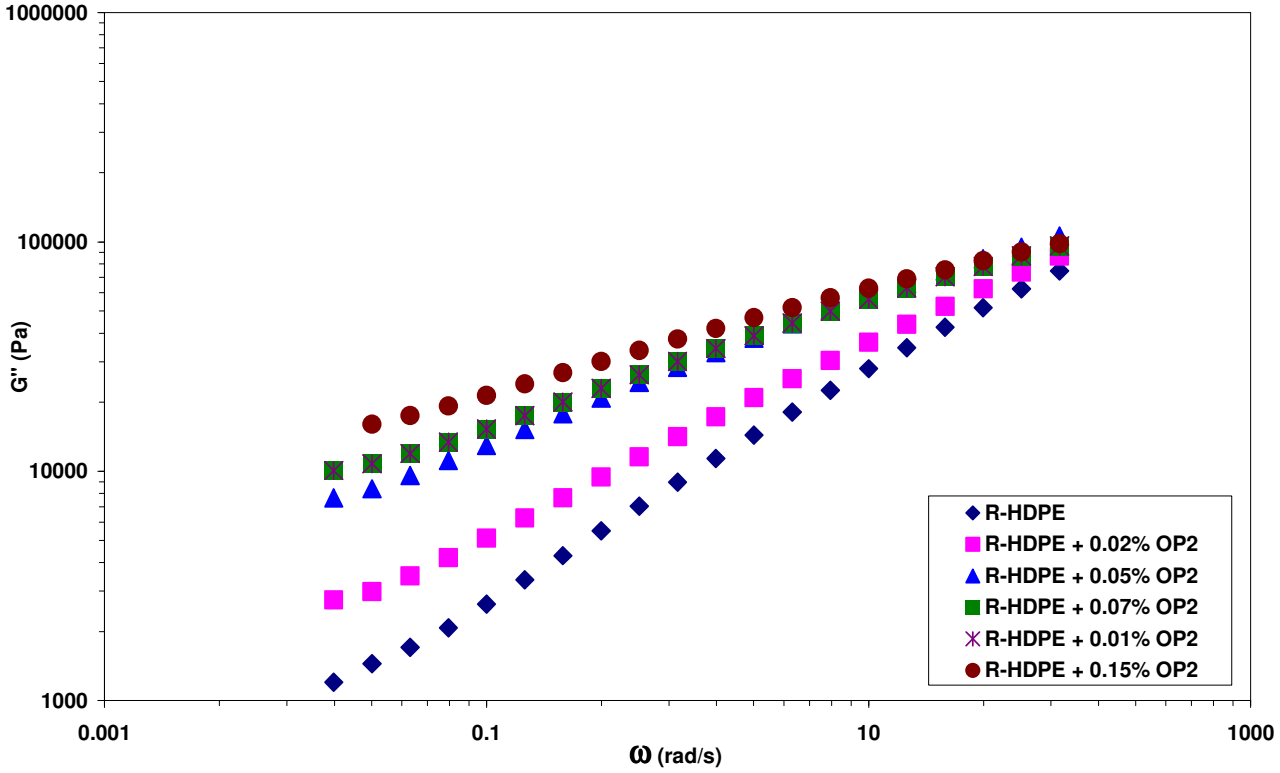


Figure 4-5 Dynamic frequency sweep results for R-HDPE modified by OP2 (a) storage modulus (G') (b) Loss modulus (G")

Figures 4-6 and figure 4-7 show the low-frequency (0.03 rad/s and 0.1 rad/s) response of G' as a function of peroxide concentrations for V-HDPE modified by DCP and OP2 respectively. It can be seen that the peroxide concentrations have significant effect on G' at low frequency. The linear polymer backbone is not capable of storing energy because of fast relaxation spectrum (table 4-3); and relaxation spectrum was higher for long chain branched V-HDPE and R-HDPE (table 4-3). It implies that capability to store energy is higher than the dissipation and hence, storage moduli enhanced with degree of branching. This effect was more pronounced at lower frequency because of appearance of the effects of inherent properties, such as molecular weight distribution, relaxation modulus, of the modified polymer which played significant role at lower frequency. Moreover, figure 4-7 also proves higher degree of branching for V-HDPE modified by OP2 and strengthens the proven efficiency of OP2 in terms of degree of crosslinking or branching.

Figures 4-8 and 4-9 show the G' as a function of peroxide concentrations' for R-HDPE modified by DCP and OP2 in the low frequency range (0.03 rad/s and 0.1 rad/s) respectively. Enhancements in the G' was observed at all lower frequencies presented. Significantly higher enhancements were observed for R-HDPE modified by both peroxides than modified V-HDPE (figures 4-6 and 4-7). Branching adds an additional mode of relaxation which was not present in the linear material or un-modified material at lower frequencies. Higher values of G' in the low frequency region for both cases (R-HDPE + DCP and R-HDPE + OP2) compared to the values of modified V-HDPE with DCP and OP2 reflects the presence of carbon black as stabilizer coupled with long chain branching produced by both peroxides.

The moduli of peroxide modified virgin and recycled HDPE have weaker frequency dependencies than those of unmodified virgin and recycled HDPE, implying a slower relaxation of polymer chains caused by long chain branching (LCB). For monodisperse polymers or copolymers, the expected slopes of the G' and G" curves at the terminal zones will be 2 ($G' \propto \omega^2$) and 1($G" \propto \omega$) respectively. Deviations from these two values, i.e., smaller slope values, indicate the broadening of MWD and the existence of Long chain branching (LCB). Owing to the limited range of low frequency examined, none of our materials reached expected limiting behaviour. As an approximation, the slopes of G' and G" at low frequency can reflect these deviations. Thus, these slopes of G' and G" for virgin and recycled HDPE modified by DCP and OP2 were calculated and are

summarized in tables 4-1 and 4-2**Error! Reference source not found.** respectively. For branched HDPE, indeed there were tendencies of the slopes of G' and G" to drift from the expected values of 2 and 1 respectively, when the MWD is broadened. The slopes for the peroxide modified samples deviate from the terminal slopes of G' and G", which are attributed to the introduction of LCB. Slopes of G’ becoming smaller with increasing extent of LCB is more evident from G" data. Moreover, the non-terminal behaviour of modified samples suggests that there was a longer relaxation mechanism, which can be ascribed to the long chain branches formed from radical reactions (Tian et al., 2006).

Table 4-1 Slopes of G' (a) V-HDPE and (b) R-HDPE modified by DCP and OP2 at low frequencies

V-HDPE + DCP		V-HDPE + OP2	
% of Peroxide	slope	% of Peroxide	slope
0.00	0.78	0.00	0.78
0.02	0.73	0.02	0.72
0.05	0.68	0.05	0.65
0.07	0.66	0.07	0.63
0.10	0.66	0.10	0.63
0.15	0.65	0.15	0.60

(a)

R-HDPE + DCP		R-HDPE + OP2	
% of Peroxide	Slope	% of Peroxide	slope
0.00	0.68	0.00	0.68
0.02	0.61	0.02	0.60
0.05	0.55	0.05	0.58
0.07	0.53	0.07	0.52
0.10	0.53	0.10	0.51
0.15	0.51	0.15	0.50

(b)

Table 4-2 Slopes of G" (a) V-HDPE and (b) R-HDPE modified by DCP and OP2 at low frequencies.

V-HDPE + DCP		V-HDPE + OP2	
% of Peroxide	slope	% of Peroxide	slope
0.00	0.73	0.00	0.73
0.02	0.67	0.02	0.60
0.05	0.66	0.05	0.60
0.07	0.67	0.07	0.59
0.10	0.66	0.10	0.59
0.15	0.64	0.15	0.59

(a)

R-HDPE + DCP		R-HDPE + OP2	
% of Peroxide	slope	% of Peroxide	slope
0.00	0.65	0.00	0.65
0.02	0.58	0.02	0.56
0.05	0.52	0.05	0.53
0.07	0.51	0.07	0.51
0.10	0.50	0.10	0.50
0.15	0.50	0.15	0.49

(b)

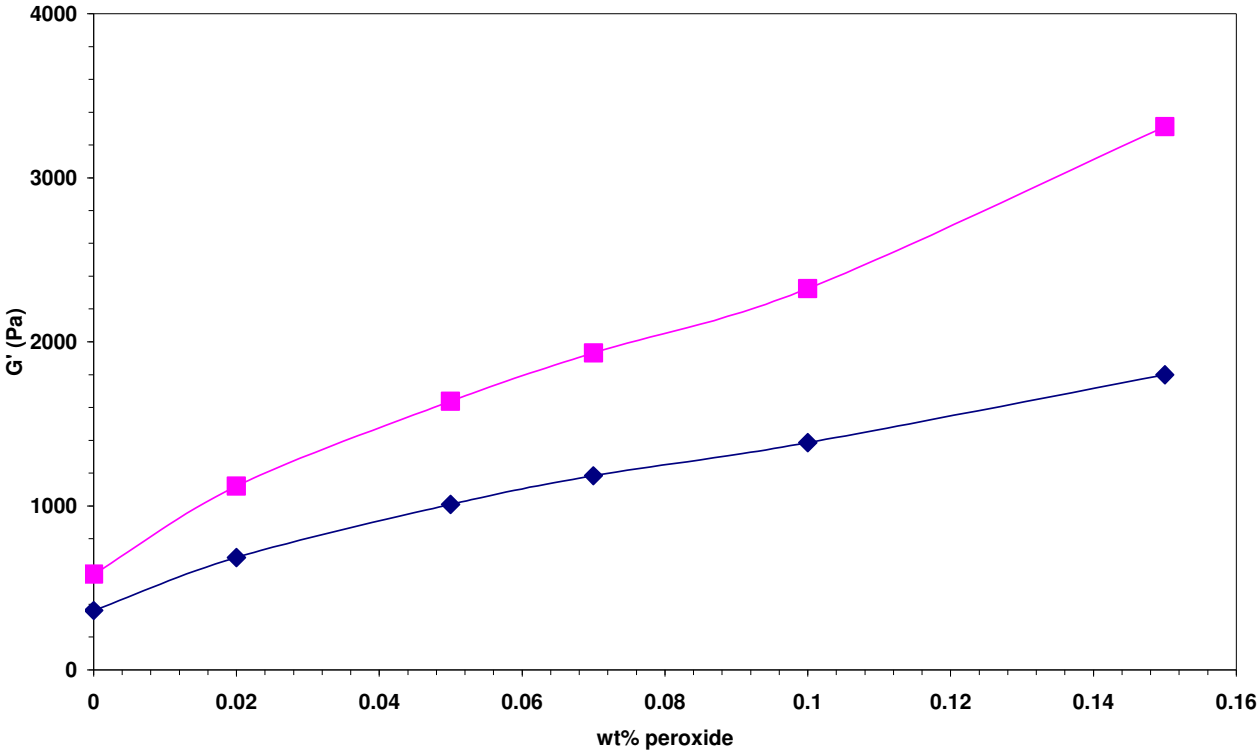


Figure 4-6 Low-frequency response of storage modulus for V-HDPE with DCP at 0.03 rad/s (♦) and 0.1 rad/s (■), temperature 190 °C

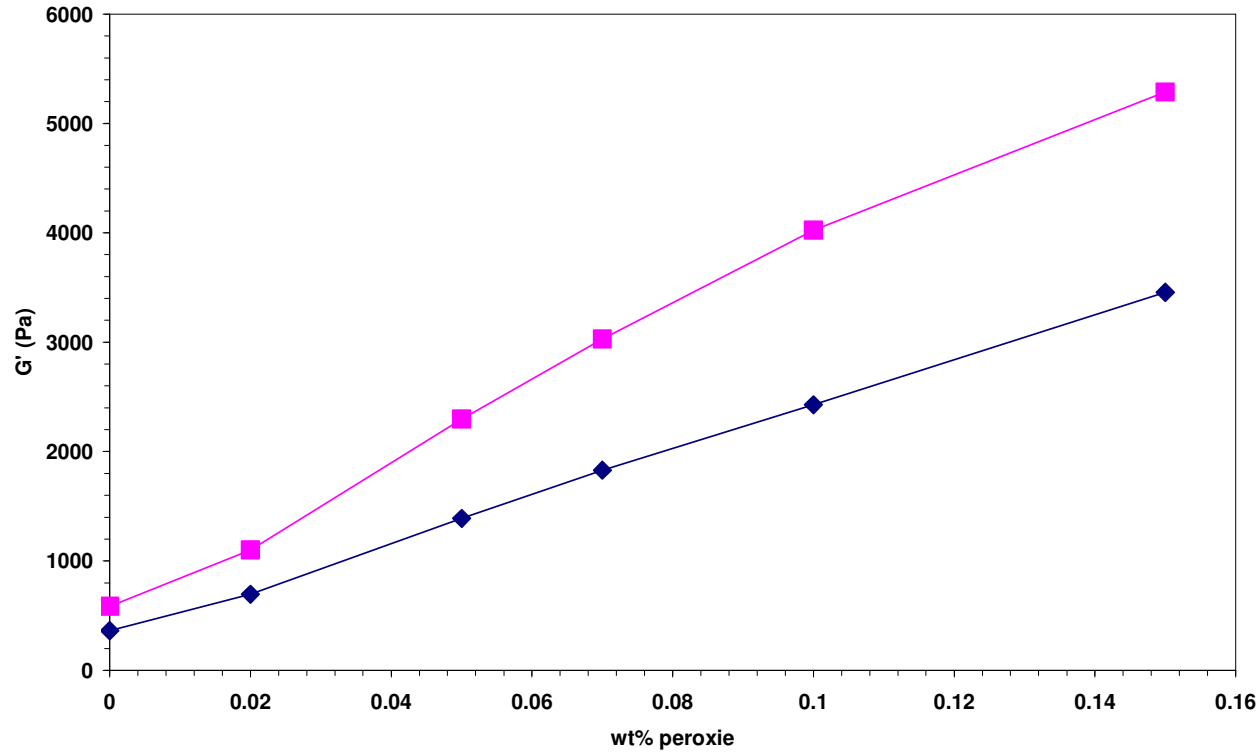


Figure 4-7 Low-frequency response of storage modulus for V-HDPE with OP2 at 0.03 rad/s (♦) and 0.1 rad/s (■), temperature 190 °C

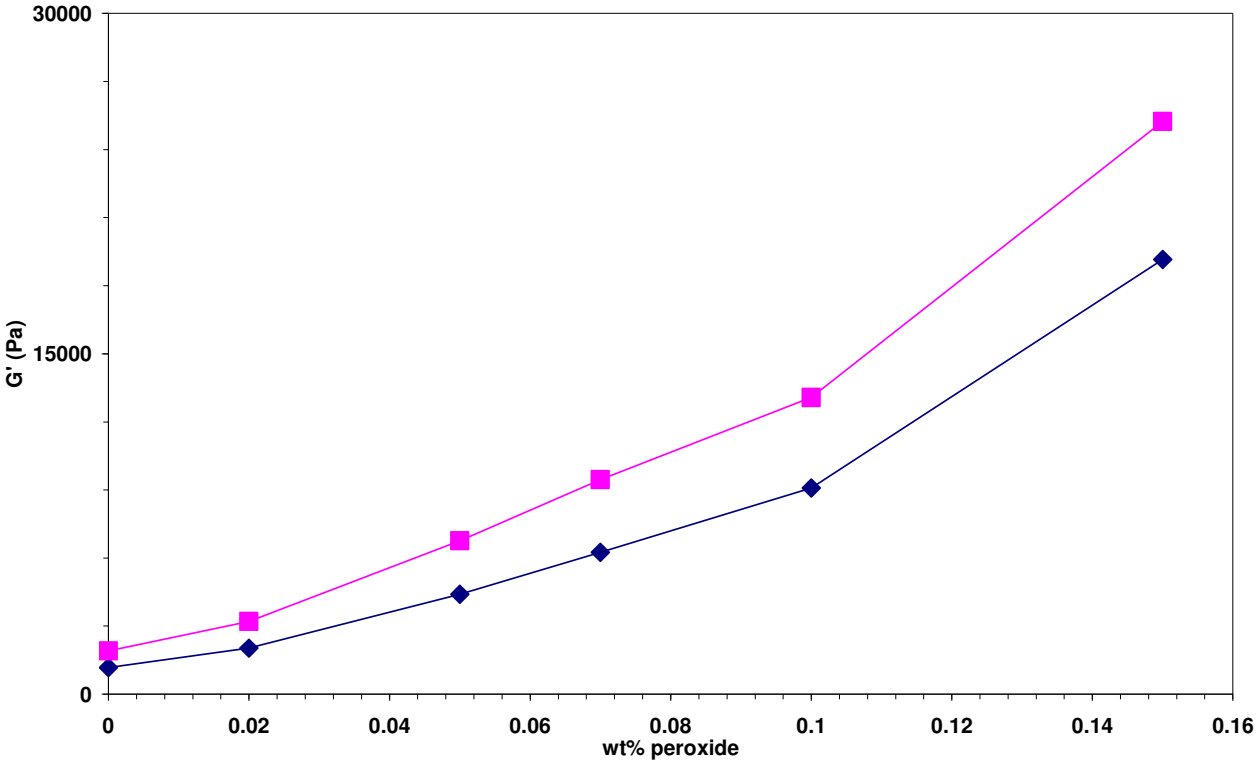


Figure 4-8 Low-frequency response of storage modulus for R-HDPE with DCP at 0.03 rad/s (♦) and 0.1 rad/s (■), temperature 190 °C

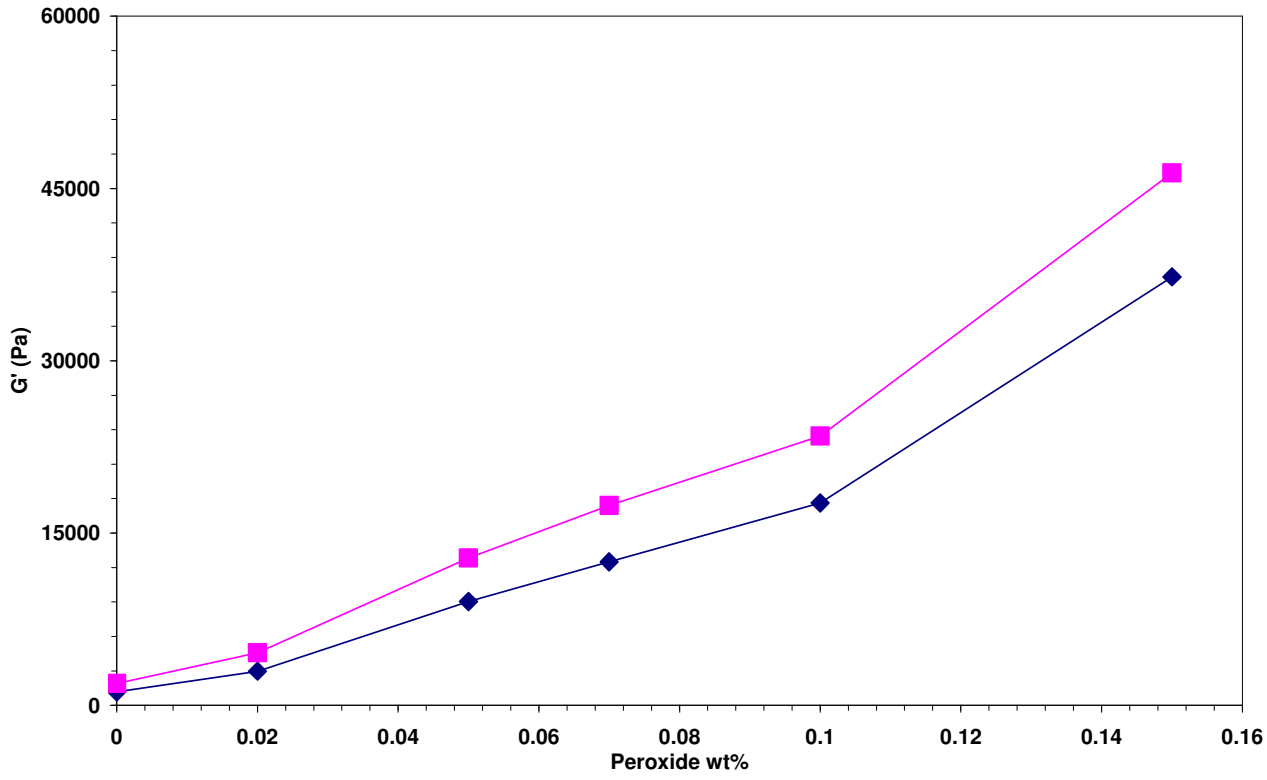


Figure 4-9 Low-frequency response of storage modulus for R-HDPE with OP2 at 0.03 rad/s (♦) and 0.1 rad/s (■), temperature 190 °C

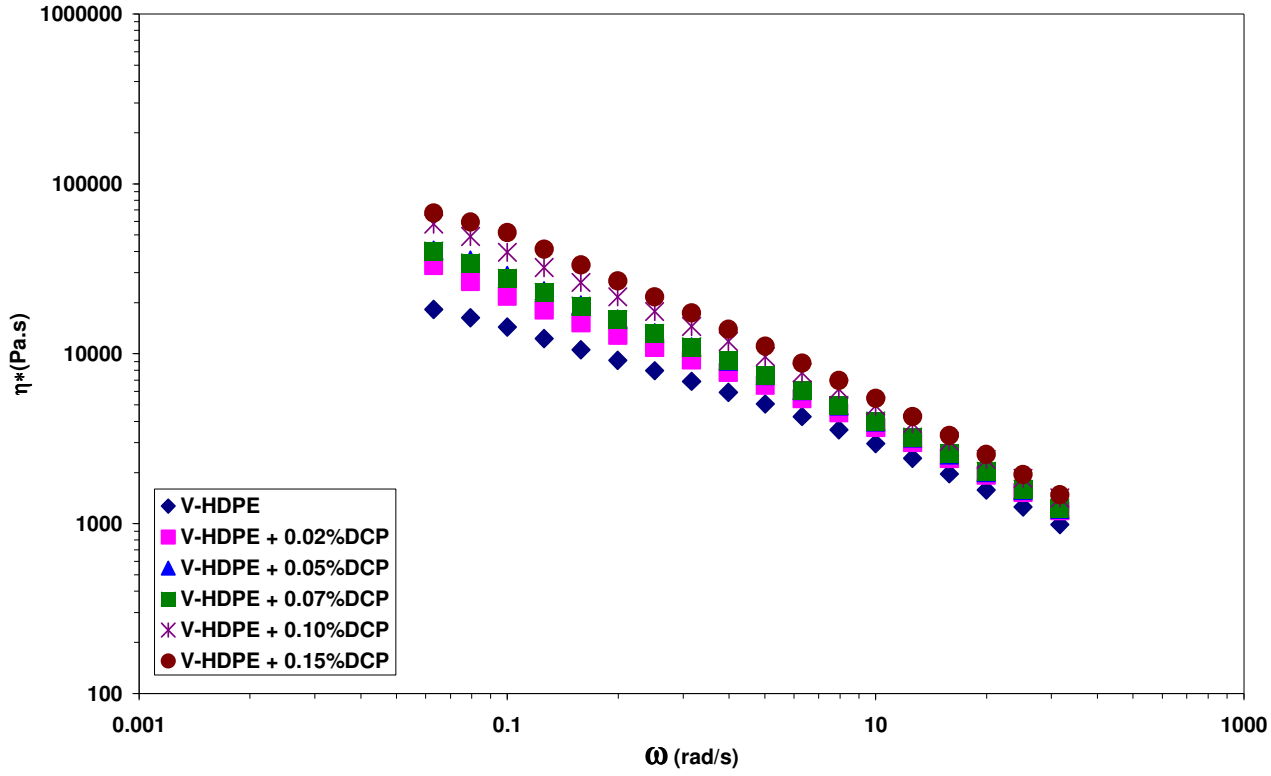


Figure 4-10 Complex viscosity profile of V-HDPE + DCP at 190 ° C

Figure 4-10 and figures A-5 to A-7 (appendix) show the complex viscosity (η^*) profiles of V-HDPE and R-HDPE modified by DCP and OP2 peroxides respectively. The complex viscosity behaviour was also affected by both peroxide compositions with V-HDPE (figure 4-10 and A-5 (appendix)). Clearly, in all the cases the modified materials showed progressive increase in complex viscosities with increase in peroxide loading at all frequencies tested. Another striking feature was their pronounced shear thinning behaviour at high frequencies for all modified materials. Cogswell (1981) reported the generalized response of a polymer melt undergoing a stretching flow under shear stress and the resulting extrudate exhibit elasticity as melt tension. He observed that, viscosity decreased as shear rate increased in the non-Newtonian regime and this response is known as shear thinning. Melt tension can decrease, remain constant or increase, depending on whether or not the polymer is a linear one with a high molecular weight, a linear one with low molecular weight, or a branched polymer. Note that a branched polymer is exceptional in that it can simultaneously have enhanced melt tension while still exhibiting shear thinning (Cogswell, 1981). Clearly, type and distribution of branching can profoundly affect the rheology and processing of polyethylenes.

Further noticeable feature in figure 4-10 is that the enhancement in complex viscosity was more pronounced at lower frequencies and this enhancement quite drastic in case of OP2 than DCP. Moreover, all the samples of V-HDPE modified by DCP followed Newtonian region at lower frequency (figure 4-10). However, all other samples (V-HDPE modified by OP2 and R-HDPE modified by DCP and OP2 both) in figures A-5 to A-7 (Appendix) followed non-Newtonian behaviour in the lower frequency region. Milas et al (2001) reported that the transition from Newtonian region to the non-Newtonian region occurred over wide range of shear rates and this transition was because of broadening in molecular weight distribution. Conversely, reducing the number of entanglements decreases the viscoelastic nature of the polymer and it behaves as a Newtonian fluid. Also, highest complex viscosity enhancement at low shear rates correlated with better processability in blow moulding and extrusion foaming by gas injection (Dealy and Wissbrun, 1990b, Quintans et al., 2000). It can be attributed to longer relaxation time mechanism. However, R-HDPE without peroxide modification also showed divergence to non-Newtonian behaviour because of carbon black in it. Polymer-filler interaction in melt state and non-Newtonian divergence have been reported for block copolymers (Larson, 2000).

Further, divergence of complex viscosity from Newtonian to non-Newtonian region at low shear rate signifies the presence of yield stress. This yield stress can be explained in terms of concentration and strengthening of modified material because of branching mechanism formed by peroxide modification. Sapieha et al (1990) reported yield stress enhancement in DCP modified-cellulose/LLDPE composites even at low concentration of peroxide. Furthermore, the authors suggested that, after critical concentration of peroxide yield stress became constant and they defined critical concentration of peroxide as 95% of yield stress obtained for given fibre content. Critical concentration of DCP was 0.01 wt% and 0.021 wt% for 23 wt% and 33 wt% of fibre respectively.

At low frequencies, a modified sample observed divergence in the viscosity as discussed earlier (figure 4-10 and figures A-5 to A-7 (appendix)). This divergence was similar to that of storage modulus as shown in (figures 4-2 (a) to 4-5 (a)), where G' diverged form Newtonian to non-Newtonian region or solid like behaviour at equilibrium moduli irrespective of frequency. Attainment of equilibrium modulus attributed to elastic nature of the modified material which shows the similar consequence observed in complex viscosity. Observations by some researchers (Carella

et al., 1986, Graessley, 1977) strengthen the proof that the divergence in G' signifies higher relaxation time for entangled polymer. Also further poof was given by Graessley (1977) that enhancement in the molecular weight or degree of entanglement or branching of the polymer chains leads to longer relaxation spectrum. Hence, it can be explained that the polymer with higher degree of branching slows down the motion of the molecules and further adjoining chains followed by entire polymer backbone. Further, this chain entanglements or crosslinking process forms strong intermolecular forces between adjacent chains.

In case of peroxide modified HDPE resin, as shown in figures 4-2 (a) to 4-5**Error! Reference source not found.** (a) that OP2 modified V-HDPE and R-HDPE showed more prominent elastic nature compared to DCP modified material. The modification method is based on the formation of oxy-radicals at higher temperatures. It is thought that, high reactivity in terms of active oxygen content of OP2 results in higher degree of entanglements. Moreover, these entanglements reduce motion of the overall polymer chains in the melt state at lower frequencies. Reduction in the chain motion cause higher relaxation time at low frequency region and when materials travelling from high frequencies to low frequencies, it store energy rather than dissipation of energy (G'>G"). Both G' and G" become equal at the crossover point of G' and G", and the corresponding frequency is known as the crossover frequency. This crossover frequency (ω_c) is inversely proportional to the characteristics relaxatation time (λ_c).

Table 4-3 shows the characteristics relaxation time as obtained from cross over point of G' and G". As shown in table 4-3, characteristics relaxatation time (λ_c) increased with peroxide loading in both modified virgin and recycled HDPE. There is no cross over points found at higher concentration of peroxide for recycled material modified by OP2. It implies that the characteristics relaxatation time is higher that other modified materials.

4.1.2.1 Effect of Peroxide Concentration on the Elastic Response of V-HDPE and R-HDPE

Elastic response of the modified material can be analysed by modified Cole-Cole plot, which is the simple representation of G' Vs G" on logarithmic scales. Modified Cole-Cole plot can also compare the differences in viscoelastic behaviour resulting from long chain mechanism.

Table 4-3 Characteristics relaxatation times for V-HDPE and R-HDPE modified by DCP and OP2 were obtained from the cross over point of G' and G".

V-HDPE		R-HDPE	
DCP (Dicumyl peroxide)		**DCP (Dicumyl peroxide)**	
Peroxide content (%)	**Characteristics Relaxation Time (s)**	**Peroxide content (%)**	**Characteristics Relaxation Time (s)**
0.00	0.0251	0.00	0.1
0.02	0.0251	0.02	0.6309
0.05	0.0630	0.05	15.8478
0.07	0.0630	0.07	15.8478
0.10	0.1584	0.10	-----
0.15	0.3981	0.15	-----

OP2 (1, 3 1, 4 Bis (tert- butylperoxyisopropyl) Benzene)		**OP2 (1, 3 1, 4 Bis (tert- butylperoxyisopropyl) Benzene)**	
Peroxide content (%)	**Characteristics Relaxation Time (s)**	**Peroxide content (%)**	**Characteristics Relaxation Time (s)**
0.00	0.0251	0.00	0.1
0.02	0.0398	0.02	1.0
0.05	0.0796	0.05	-----
0.07	0.3981	0.07	-----
0.10	0.6309	0.10	-----
0.15	1.5848	0.15	-----

Note: Equation $\lambda_c = \frac{1}{\omega_c}$ was used to calculate these values of characteristics relaxation time.

Originally, Cole-Cole plot was produced by Cole and Cole (1941) to analyse and represent complex dielectric constant data in terms of distinct relaxation copolymers response. Harrell and Nakajima (1984) also used this modified Cole-Cole plot to analyse the effects of long chain branching on the rheology of ethylene-propylene-mechanism. However, in this study, modified Cole-Cole plots on logarithmic scales were used as an empirical tool to evaluate the long chain branching effects on elastic materials. Figures 4-11 to 4-14 show the modified Cole-Cole plots for V-HDPE and R-HDPE modified by DCP and OP2 peroxides. Values of G' and G" at lower frequencies for all modified material were found to increase with peroxide concentration. Also G' showed higher increment than G" at all lower frequencies tested, indicating that, more amount of energy was stored than amount of energy dissipated by the system. The increase of G' value with increasing degree of branching was readily noticeable by the progressive shift of the respective Cole-Cole plots from unmodified material to

modified material by higher concentration of peroxides. The Cole-Cole plot curves of V-HDPE and R-HDPE samples modified by both peroxides with decreasing concentration of peroxide are shifting monotonically downwards with decreasing Polydispersity index (PI). Hence, for modified virgin and recycled HDPE, the broadening of MWD will shift the Cole-Cole plot to higher values of G' at constant values of G". Shift in the Cole-Cole plot was more noticeable at higher peroxide loading and also with OP2 modified materials.

From the molecular point of view, the high moduli region at high frequencies is related to the relaxation of short range segments of polymer chain, which may not be altered greatly by reactive extrusion due to the low peroxide concentrations used. It was also noted that in the work of Harrell and Nakajima (1984),that a single curve was obtained by varying the MW of linear polymers while keeping their MWDs and molecular structure invariant. In our system, the molecular weight, MWD and molecular architecture are all varying. The rule of forming a single curve seems to break up at lower moduli region for V-HDPE peroxide modified samples. Moreover, in case of R-HDPE samples modified by peroxide can not form single curve even at higher moduli region.

Although the existence of branching mechanism can be seen roughly from the modified Cole-Cole plots, their low sensitivities to the degree of branching can be seen in our system. This may be caused by small extents of branching. More representations of the Cole-Cole plots for different concentrations are shown in appendix (figures A-8 to A-11 (appendix)) which is more sensitive to the change in molecular structures.

Figures A-8 to A-11 (appendix) show plot of tan δ as a function of complex modulus G* of V-HDPE and R-HDPE modified by both peroxides respectively. Tan δ is decreased with increasing polydispersity (PI). For modified materials, curves are drifting downwards with increasing PI and indicates that the broadening of MWD will shift the curves to lower values of tan δ at constant values of G*.

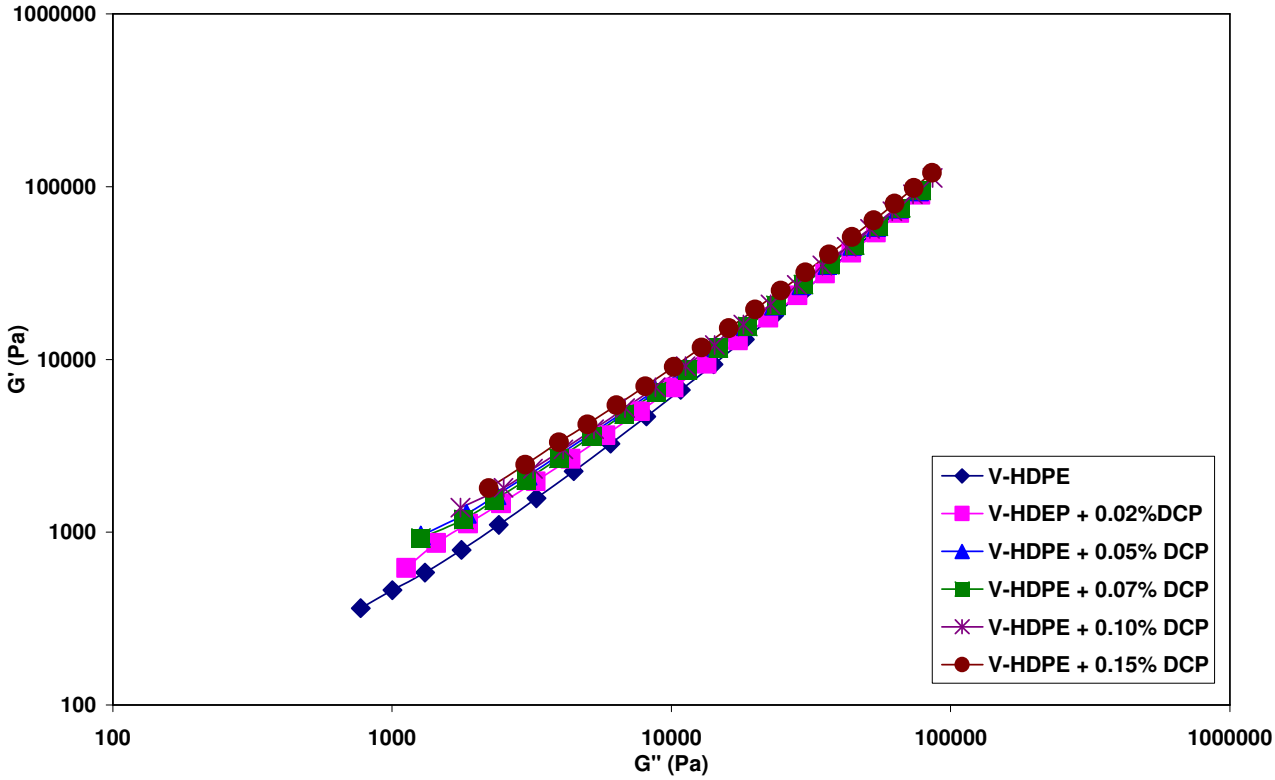


Figure 4-11 Modified Cole-Cole plots of V-HDPE modified by DCP at 190 ° C

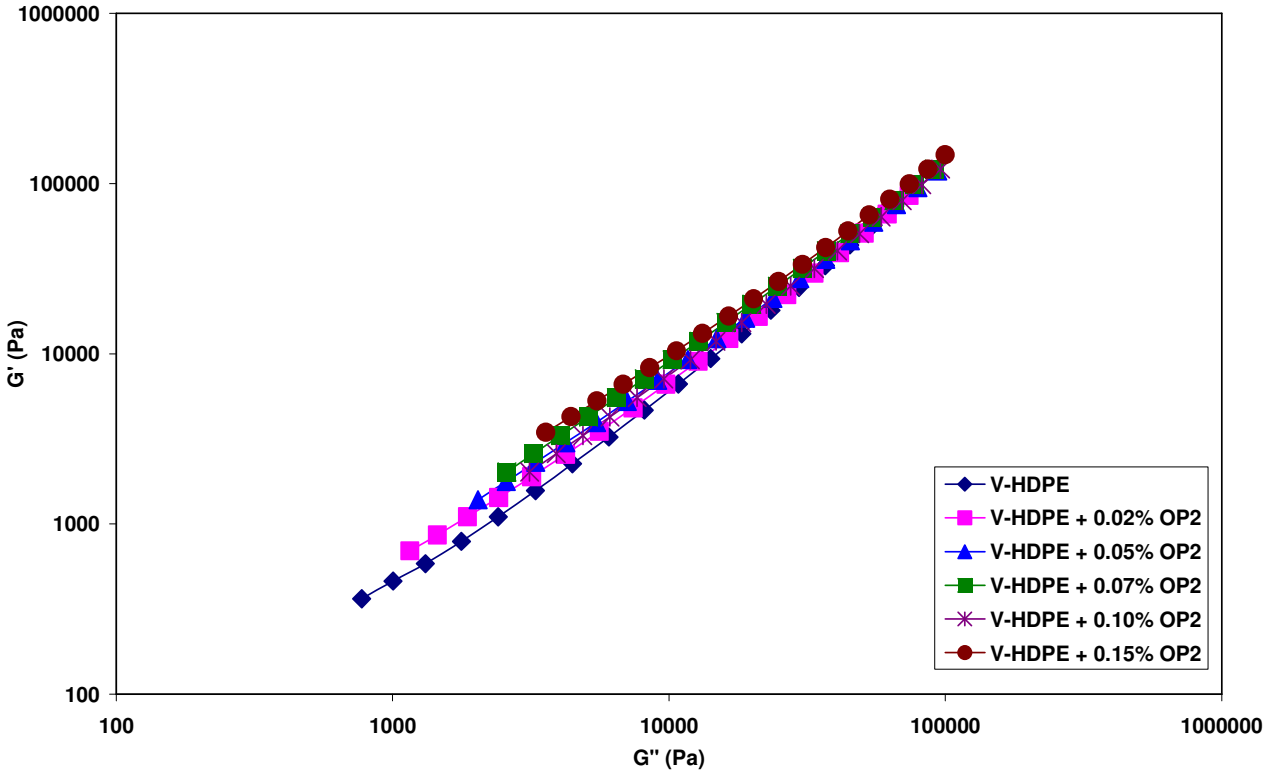


Figure 4-12 Modified Cole-Cole plots of V-HDPE modified by OP2 at 190 ° C

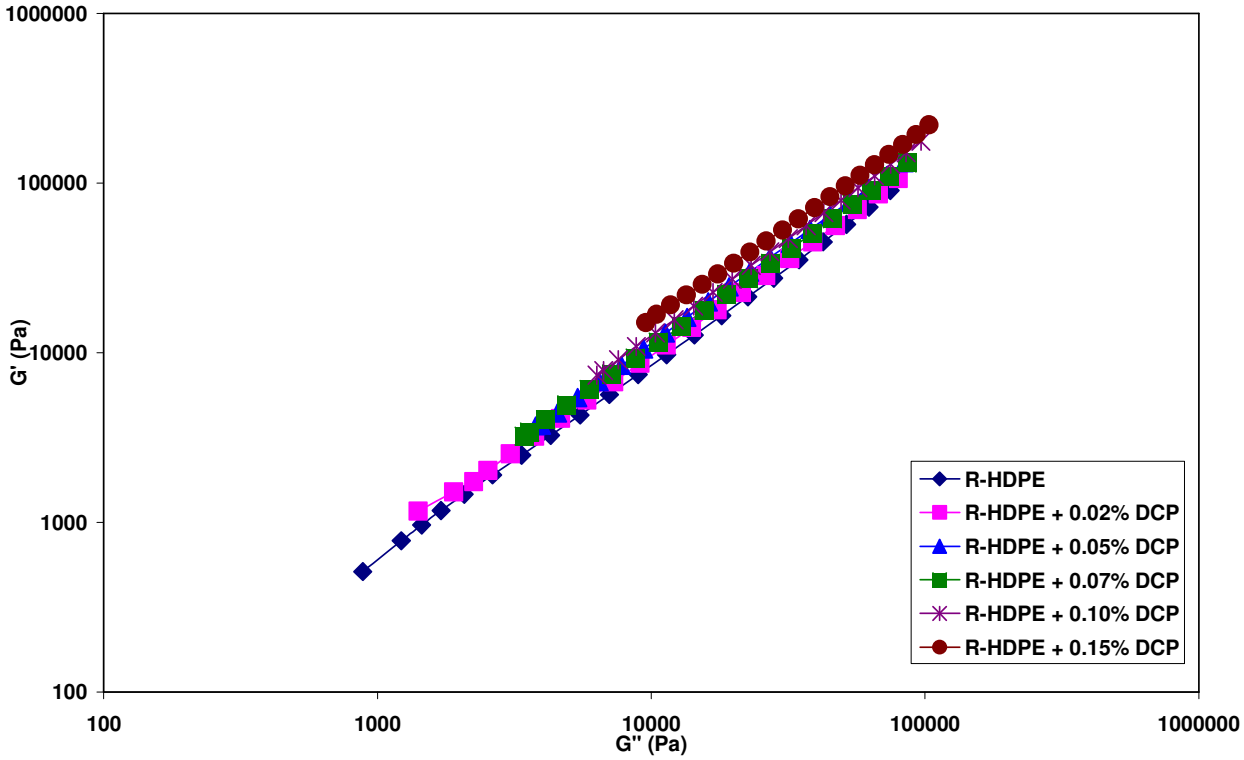


Figure 4-13 Modified Cole-Cole plots of R-HDPE modified by DCP at 190 ° C

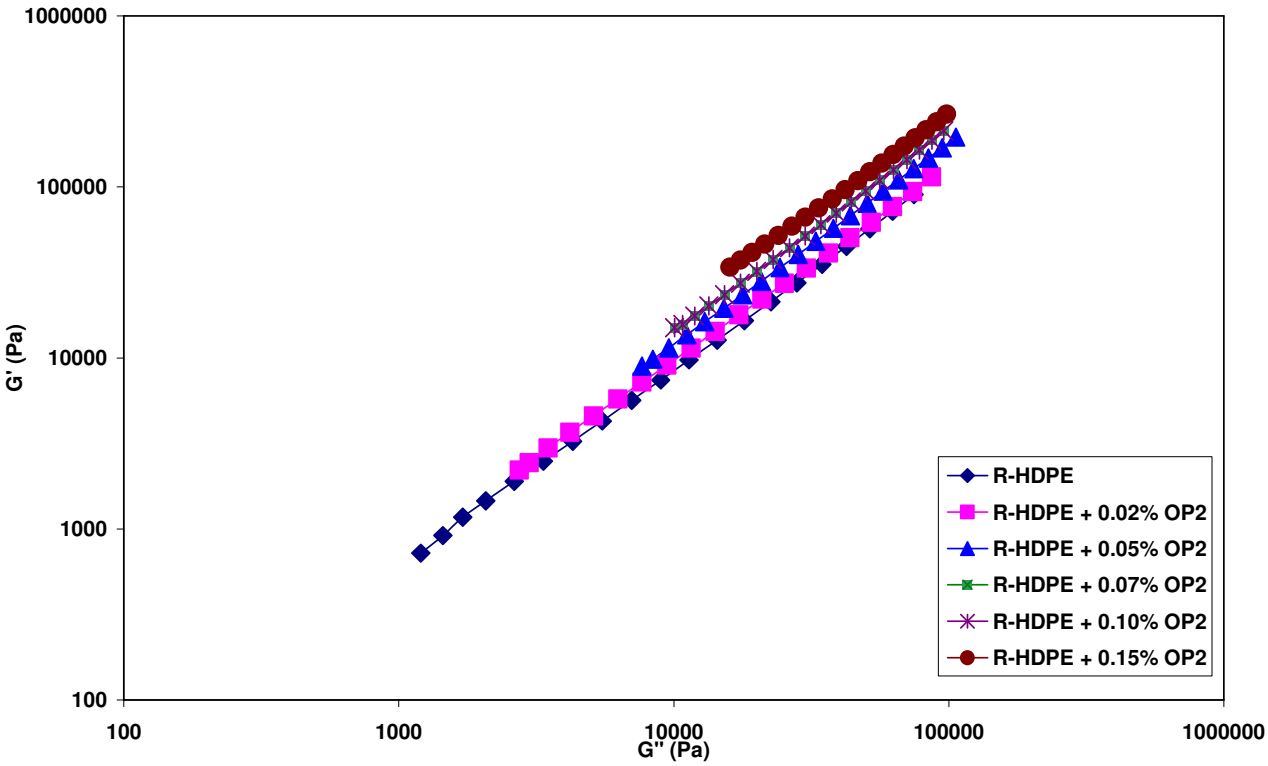


Figure 4-14 Modified Cole-Cole plots of R-HDPE modified by OP2 at 190 ° C

4.2 *UNIAXIAL MELT EXTENSIONAL MEASUREMENT*

4.2.1. Göttfert Rheotens Melt Strength Tester

The Rheotens tests for reactively extruded virgin and recycled materials with two different organic peroxides and without peroxides were conducted at a mass flow rate of 4.1 x 10^{-3} kg/sec and nip roller acceleration of 12 mm/sec^2. Temperature was maintained at 200 °C at the die exit. Figures 4-15**Error! Reference source not found.** to 4-18 show the draw down force versus draw ratio relationship obtained for the untreated (0 wt% of organic peroxide) and reactively extruded V-HDPE + DCP, V-HDPE + OP2, R-HDPE + DCP, R-HDPE + OP2 systems respectively. Melt strength represents the maximum tension that can be applied to the melt without rupture or tearing. It is a relative measure of the extensional strength of the material. Single screw Haake extruder was used to extrude a polymer and the strand was pulled till rupture by a pair of rollers. The maximum draw ratio is regarded as the extensibility or drawability of the melt under examination. Drawability or extensibility gives an indication of how much the melt can be stretched by the nip rollers prior to breakage or the onset of instability (Prasad et al., 2005).

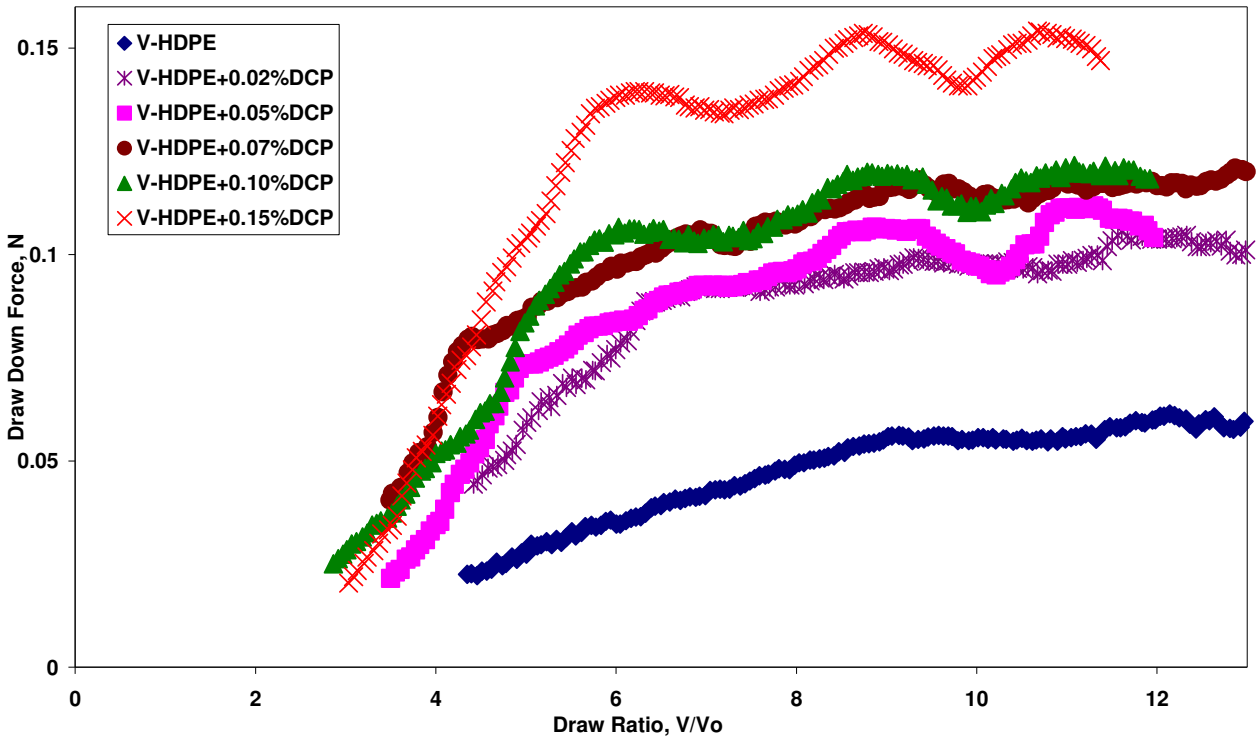


Figure 4-15 Force- Draw Ratio profile for V-HDPE with DCP carried out using Göttfert Rheotens melt strength tester (Buchen, Germany) at 200 ° C

For V-HDPE with DCP (figure 4-15**Error! Reference source not found.**) and with OP2 (figure 4-16), it is observed that both drawability and draw down force of the modified systems were considerably higher than that of the unmodified V-HDPE. The melt strength of the samples increased with peroxide loadings (figure 4-19). The significant increase in melt strength and drawability can be attributed to the presence of long chain branching. These results support the shear rheological results to a certain extent since both showed rise in melt properties with increase in peroxide loading. Previous work (Lem and Han, 1982) has also shown that the peroxide added to the polymer results in extended polymer chains (especially, the long chain molecules) giving rise to larger molecules and also presented the evidence that the degree of long-chain branching is increased in the presence of dicumyl peroxide free radicals. Moreover, when polymer chains are subjected to peroxide free radicals, dissociation of C-C bonds can occur simultaneously with crosslinking. Increase in melt strength was more noticeable with V-HDPE modified by 1, 3 1, 4 Bis (tert- butylperoxyisopropyl) Benzene (OP2) than by dicumyl peroxide (DCP) (figure 4-16). In addition, there was significant increase in melt strength (for both organic peroxides) at 0.15 wt%; however draw resonances were experienced at higher concentrations of both organic peroxides with V-HDPE (figures 4-15 and 4-16). Draw resonance is defined by periodic fluctuations in the dimeter of the stretched filament just before its breakage point in stretched condition.

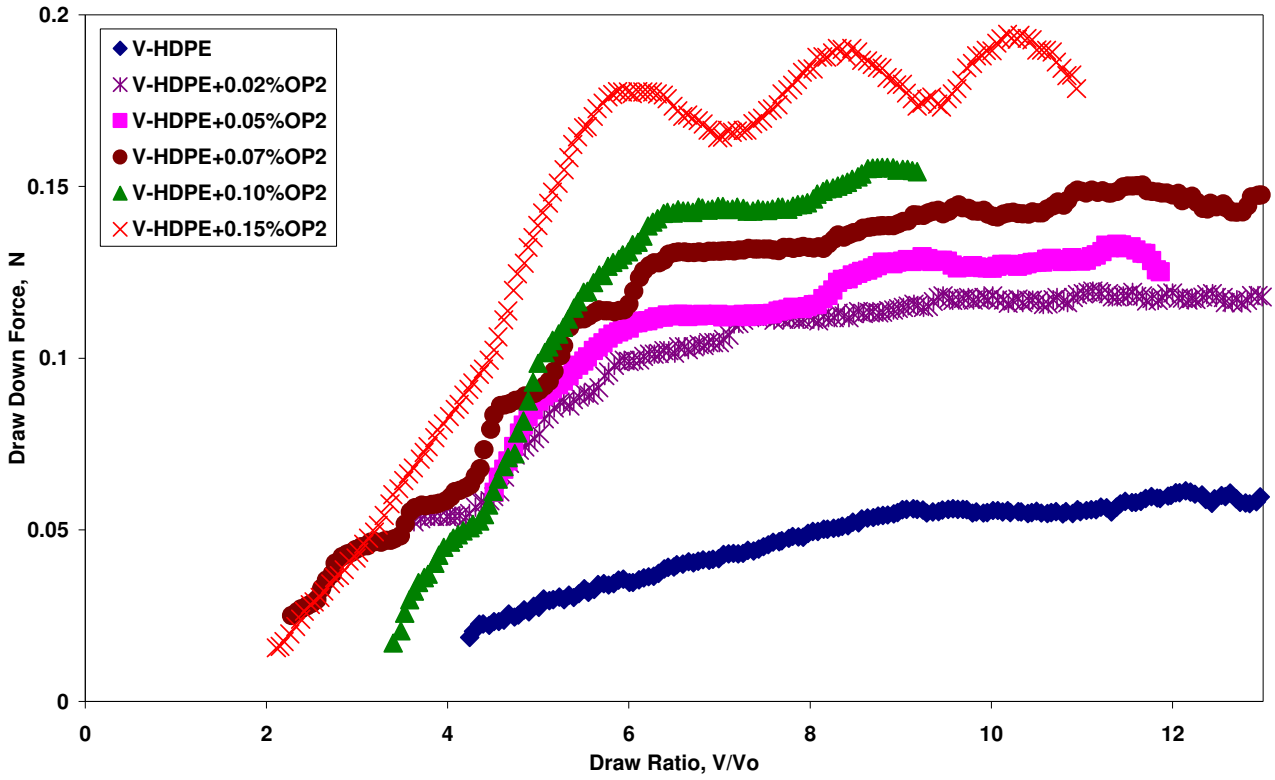


Figure 4-16 Force- Draw Ratio profile for V-HDPE with OP2 carried out using Göttfert Rheotens melt strength tester (Buchen, Germany) at 200 ° C

Figures 4-17 and 4-18 show the draw down force–draw ratio curves obtained for R-HDPE with DCP and OP2 peroxides. These figures show that as draw ratio (or nip roller velocity) was increased, the draw force or melt tension increased with the increase in organic peroxide composition. As expected, peroxides are used to create extended chain mechanism within the compositions and because of higher level of long chain branching, melt strength was increased. Mackay and Astarita (1997) reported that melt flow index (MFI) decreased with increased peroxide content or increased long chain branching in reactive extrusion of LLDPE and lower MFI polymers are likely to have longer molecular chains and these long chain molecules can create more entanglements in the polymer structure. Polymers with higher degree of entanglements will have higher resistance to extensional deformation or higher melt strength (Lau et al., 1998, Ariawan et al., 2001, Wagner et al., 1996). Increases in melt strength were more prominent with R-HDPE modified with both organic peroxides because of the presence of carbon black in it. Lobe and White (1979) explained the same phenomenon using polystyrene (PS) filled with carbon black. They reported that the filled systems such as these have high viscosities compared to the unfilled system at low shear rates. Large amount of force required stretching them with nip rollers and this leads to greater draw

down force (melt strength) of the drawn filament under the test conditions. With filled system on the other hand, extensibility found to be decreased with enhancement in melt strength because filled systems provide greater resistance to extension compared to unfilled system. Moreover, few authors (Kraus, 1965b, Bachmann et al., 1959, Kraus, 1965a) have studied the nature of interaction of filler in carbon-black filled rubbers, and found that van der Waals forces play significant role in the interaction between filler and polymer matrix. In addition, Watson (1965) reported that there was chemical grafting between carbon black and rubber. Free radical mechanism is the process by which polymer molecules grafted to carbon black surfaces, as carbon black is an efficient free radical acceptor. The high degree of bonding formed by such chemical grafting probably contributes to the extraordinary melt strength of these materials.

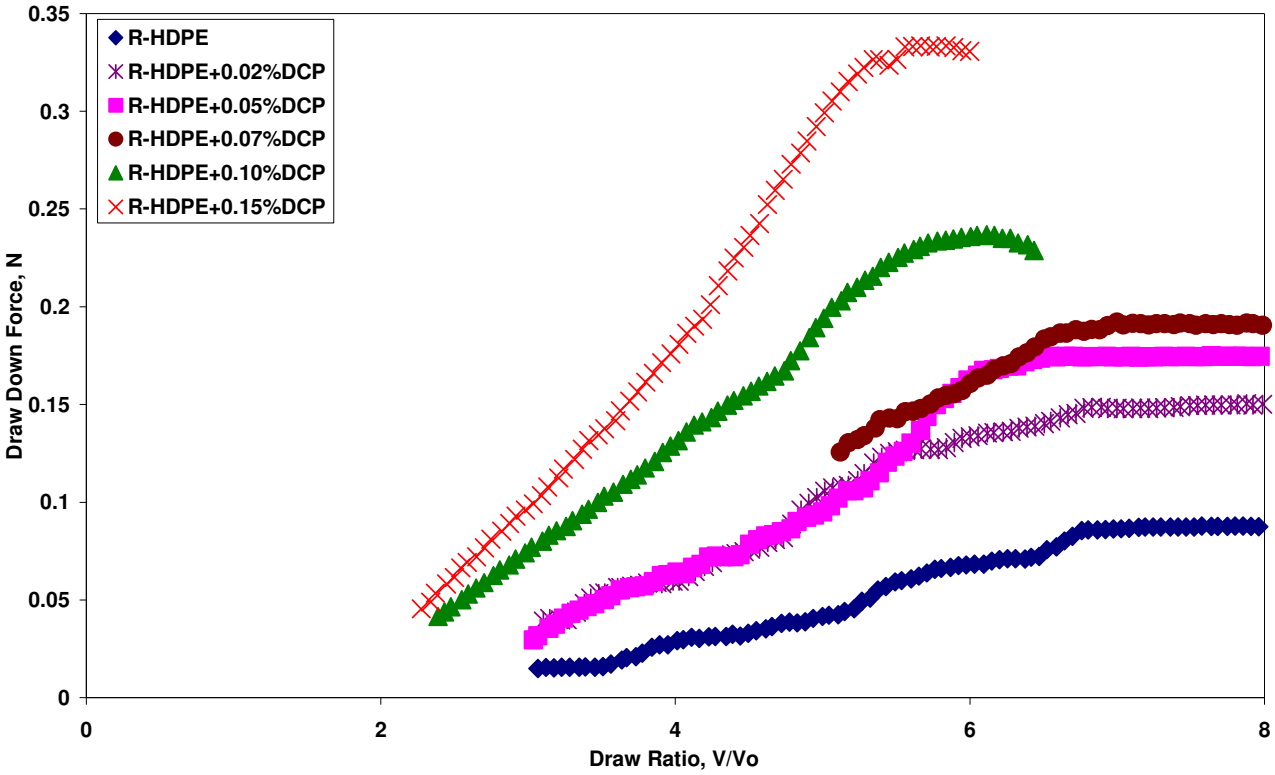


Figure 4-17 Force- Draw Ratio profile for R-HDPE with DCP carried out using Göttfert Rheotens melt strength tester (Buchen, Germany) at 200 ° C

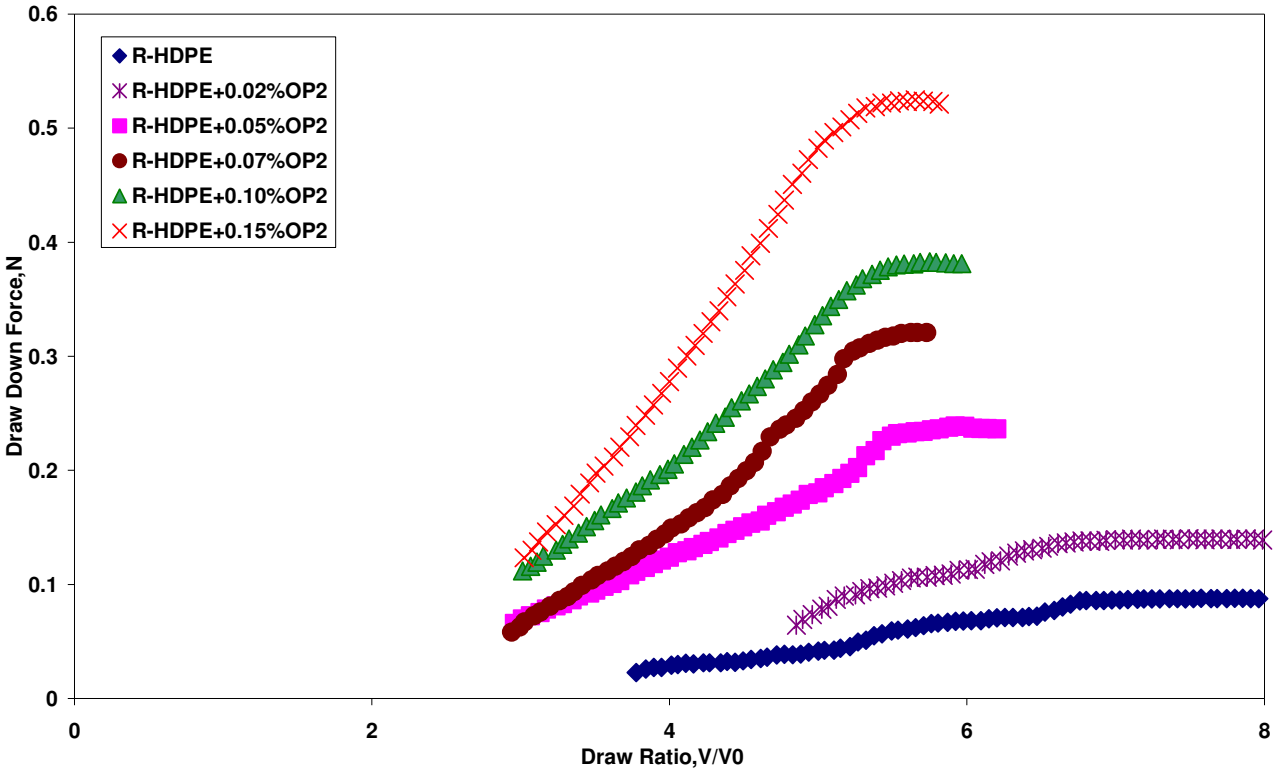


Figure 4-18 Force- Draw Ratio profile for R-HDPE with OP2 carried out using Göttfert Rheotens melt strength tester (Buchen, Germany) at 200 ° C

Extensional deformations (as a free surface deformation) are important in several polymer processing operations including blow moulding, vacuum forming, melt spinning, and extrusion (as a confined flow during convergence) (Mackay and Astarita, 1997). By drawing an extruded polymer strand between rotating rollers in Göttfert Rheotens tester is the relatively simple test that approximates the behaviour occurring during high strain rate processing operations. Note that the extensional strain was determined at the nip rollers and not along the molten fibre. The melt strength test conducted with the Rheotens apparatus does not provide a well-defined rheological parameter, as both strain and temperature are non-uniform in the melt strand.

Few authors (Laun and Schuch, 1989, Muke et al., 2001b, McInerney et al., 2003) reported proportional relationship between melt strength and extensional viscosity. An increase in one is equivalent to the increase in other. Comparisons were made between draw down force-extensibility profile and their corresponding extensional viscosity-extensional strain profiles. This profile shown in figures 4-20 to 4-23 demonstrated that, increase in draw down force has a subsequent increase in extensional viscosities at lower strains. The apparent extensional viscosities and extensional strains presented in

figures 4-20 to 4-23 were calculated from equations 3.6 to 3.9 as discussed in chapter 3. Cotten (1980) reported that at slow relaxation time, magnitude of extrusion shrinkage and extensional viscosity increases in filled systems. The author explained extrusion shrinkage in terms of molecular disorientation for the case of carbon black filled rubber stock. They also reported (Cotten and Thiele, 1978) that the extensional viscosity depends also on loading and morphology (size and shape) of filler aggregates in the filled system. This is clearly demonstrated in our system that extensional viscosities of R-HDPE (filled with low amount of carbon black) compositions with both peroxide showing greater improvements than virgin counterparts. Some researchers (Gotsis et al., 2004a, Spitael and Macosko, 2004) have reported an increase of extensional viscosity at lower strain. This behaviour showed strain hardening due to the formation of long chain branching mechanism. Similar observations were made with all the compositions of V-HDPE and R-HDPE with both peroxides.

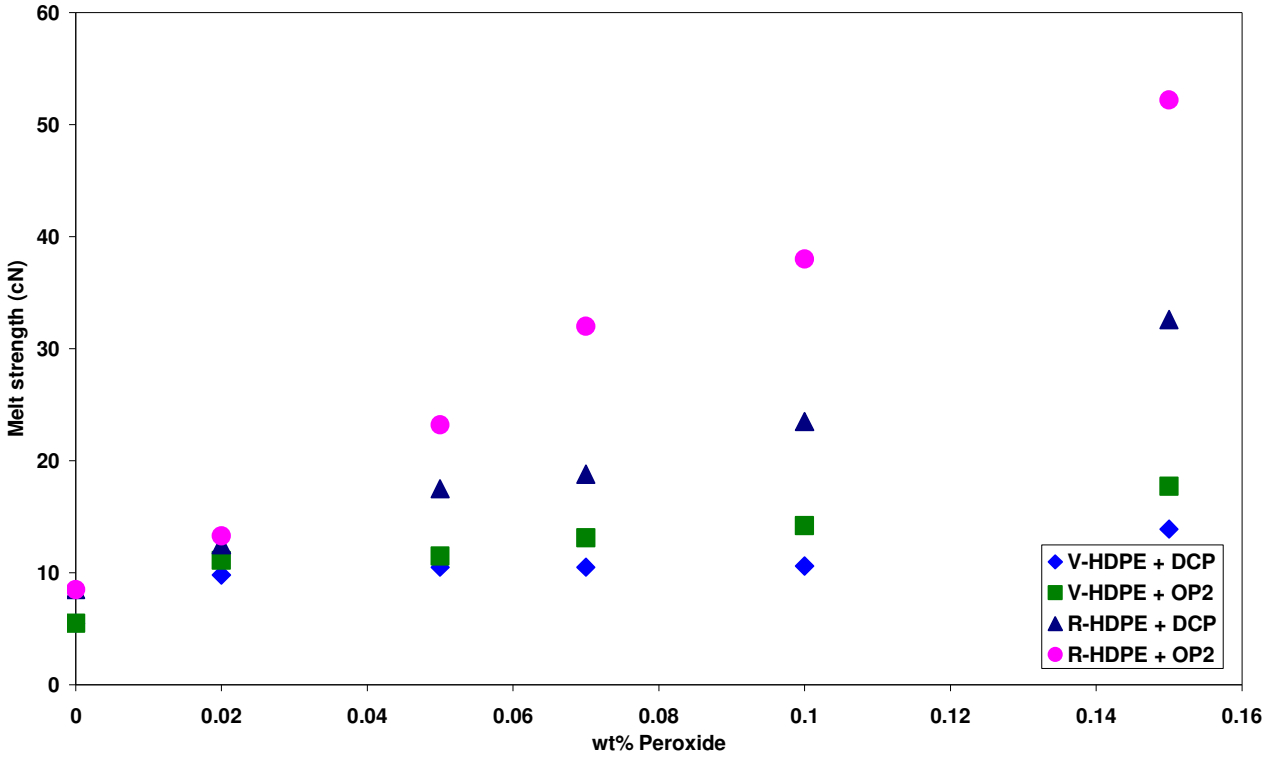


Figure 4-19 Melt strengths of unmodified and modified V-HDPE and R-HDPE as a function of peroxides wt%

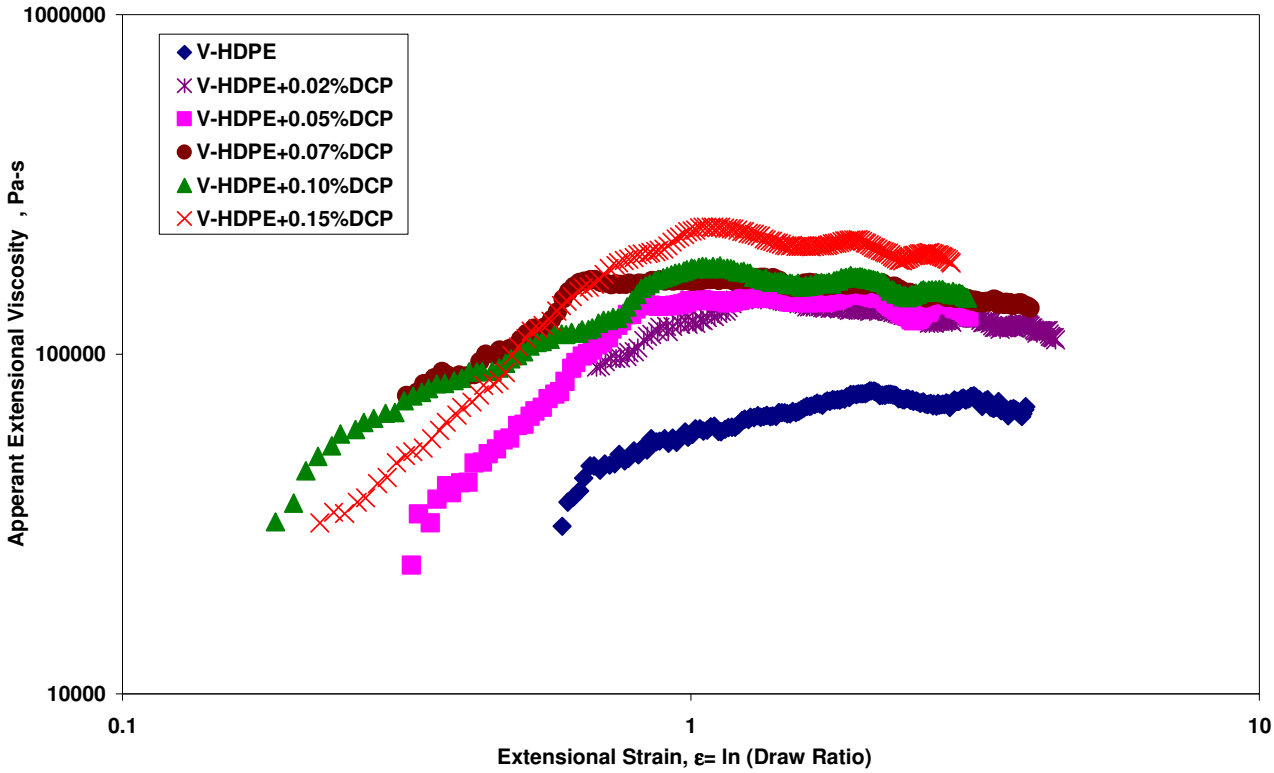


Figure 4-20 Apparent Extensional Viscosity profile of V-HDPE with DCP using Göttfert Rheotens melt strength tester (Buchen, Germany) at 200 ° C

There was a decrease in hydrodynamic stability of material with increase in peroxide loading at high draw ratio was observed (figures 4-15**Error! Reference source not found.** and 4-16); this instability is an indication of draw resonance. Draw resonance is characterised by instability due to the variations in the diameter of the strand at force exceed beyond the critical value of draw ratio (V/Vo) in the force-draw ratio profile; where V is the velocity of nip rollers and Vo is the velocity of the strand at die exit. The critical draw ratio is also a sign of necking (ductile failure). In addition, draw resonance is one of the most influencing factors affecting the processing for instance blow moulding, vacuum forming, and film casting and fibre spinning (Cogswell, 1981). White and Tanaka (1981) reported critical values of V/Vo at which draw resonance occurred for PS, high impact polystyrene (HIPS), PP, HDPE and LDPE. Flow instabilities (draw resonance) are usually experienced when extensional viscosity decreases as stress increases (White and Minoshima, 1981); modified V-HDPE at higher peroxide compositions (figures 4-15 and**Error! Reference source not found.** 4-16) shows the same trend.

However, draw resonance was not experienced with compositions of R-HDPE with both peroxides (figures 4-17 and 4-18) due to the presence of surface cracks. Since the

extrudate which acted as stress concentrators that led to the fracture of the filament without draw resonance and at the same time it can be deduced that the peroxide addition improved rheological properties to greater extent but processing limitations like draw resonance and necking (ductile failure) narrowed the processing window.

Some authors (Muke et al., 2001a, Muke et al., 2001c, Kao et al., 2002, Prasad et al., 2004) concentrated on low strain (similar with the strain at which strain hardening occurs in extensional viscosity measurement) region and calculated initial slope of the Rheotens flow (draw down force–time) curve which may give very important information to processability of the polymer. According to these authors, initial slope may be able to explain strain hardening properties since it is in the lower strain region. Branching also has great influence on elongational or extensional viscosity and strain hardening. For example, Gotsis et al (2004a) reported monotonic growth in elongational viscosity of polypropylene initially but with the peroxide modification, accelerated growth in viscosity and initial slope was reported. This region is called as strain hardening region.

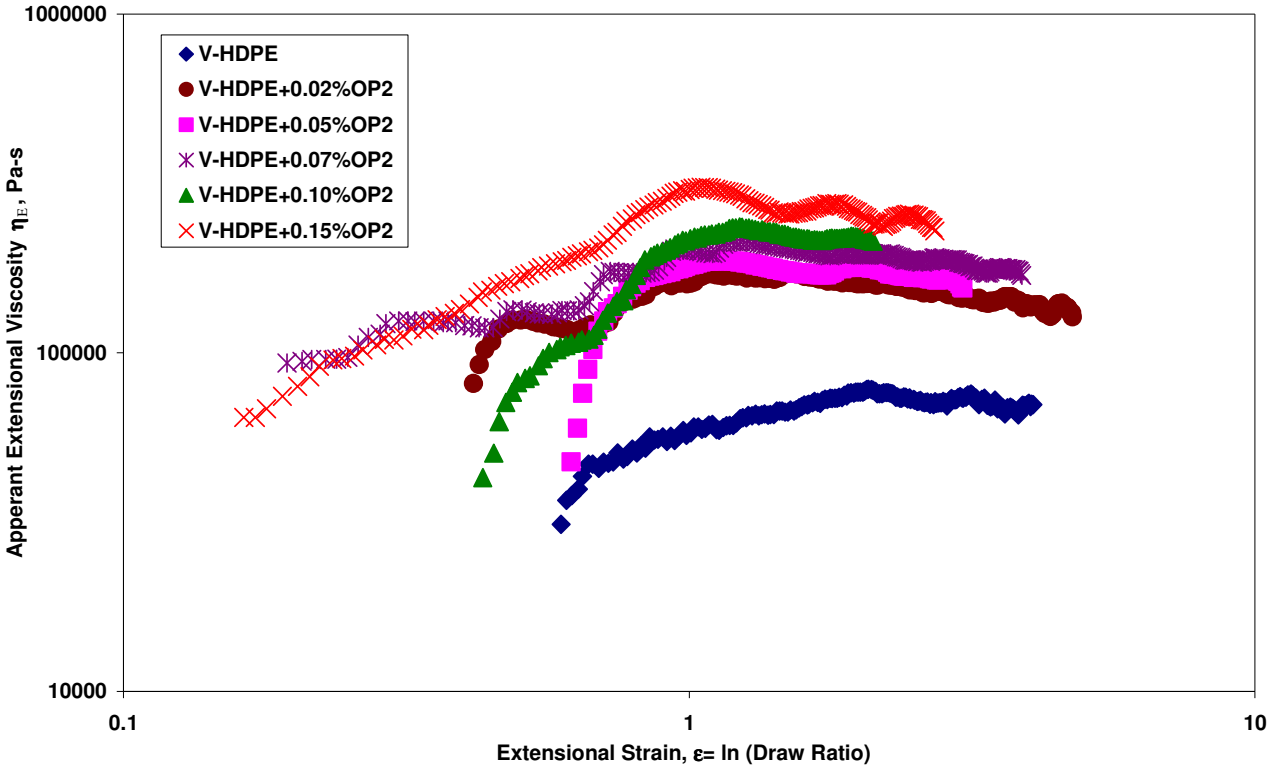


Figure 4-21 Apparent Extensional Viscosity profile of V-HDPE with OP2 using Göttfert Rheotens melt strength tester (Buchen, Germany) at 200 ° C

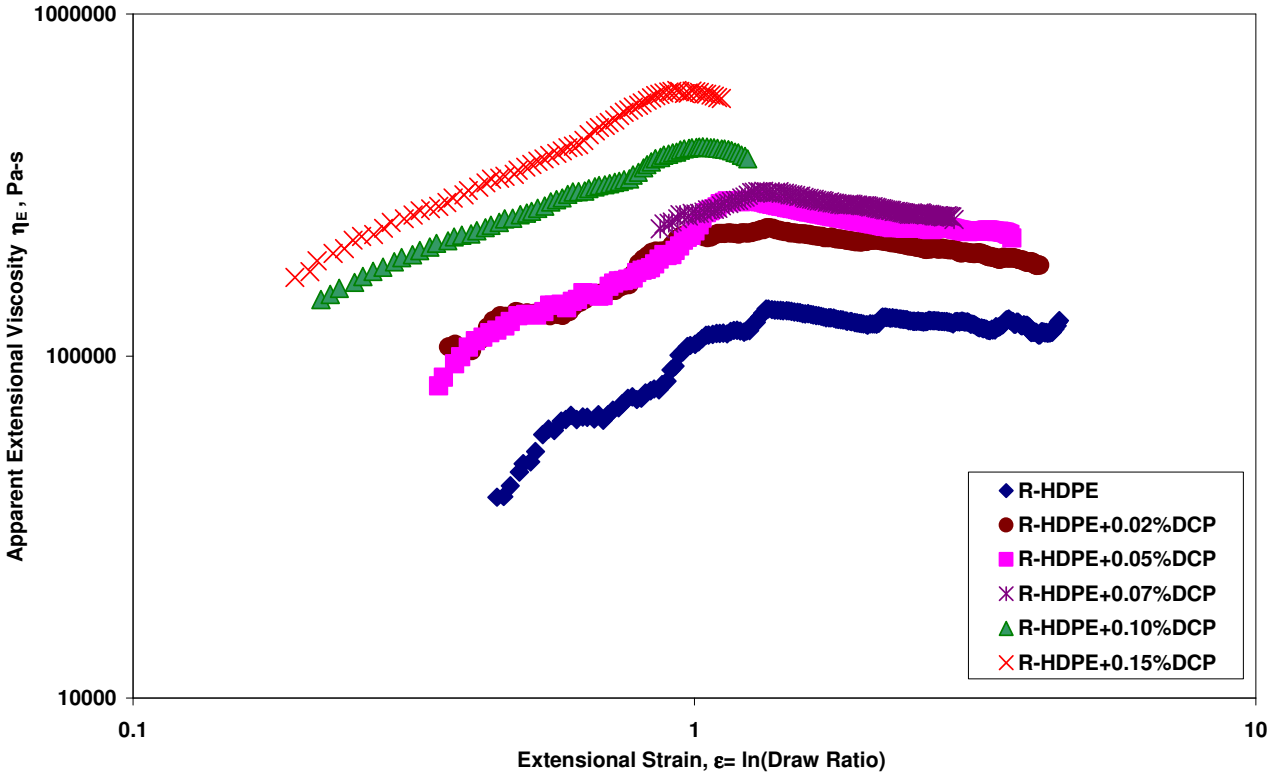


Figure 4-22 Apparent Extensional Viscosity profile of R-HDPE with DCP using Göttfert Rheotens melt strength tester (Buchen, Germany) at 200 ° C

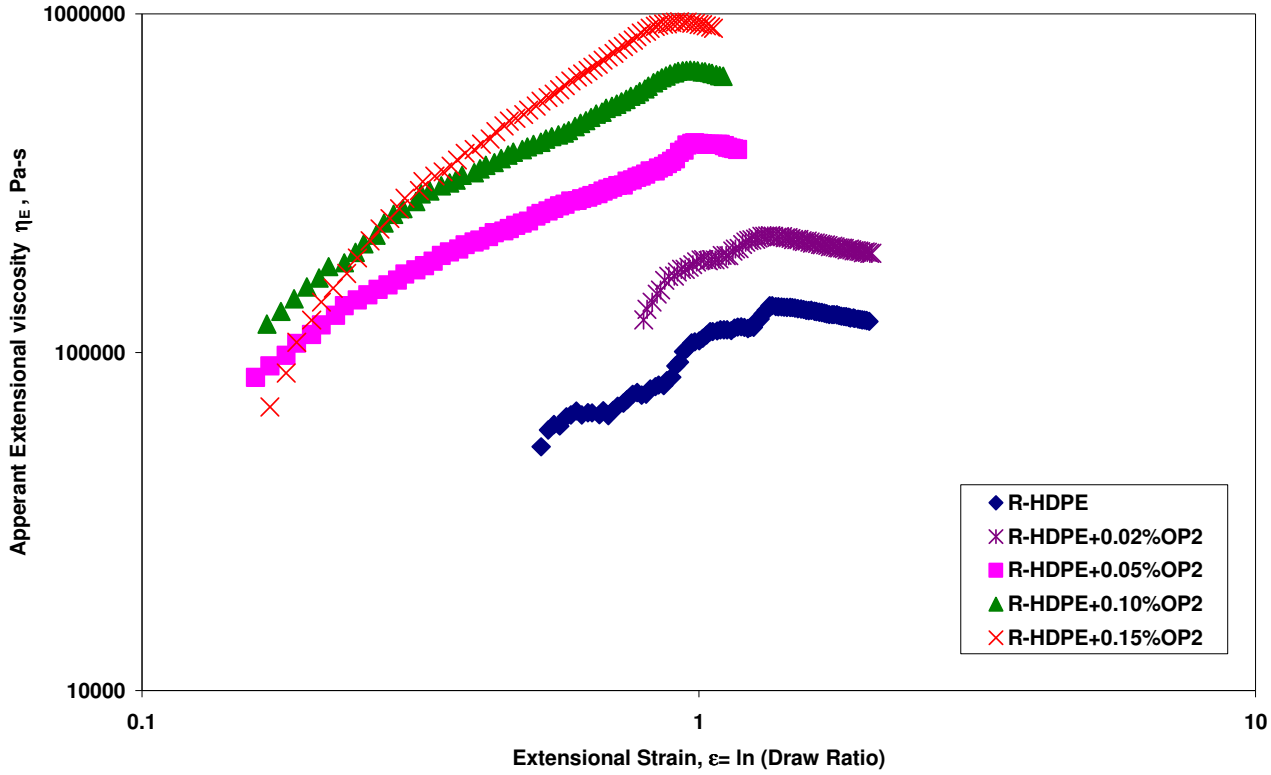


Figure 4-23 Apparent Extensional Viscosity profile of R-HDPE with OP2 using Göttfert Rheotens melt strength tester (Buchen, Germany) at 200 ° C

Figure 4-24 shows the initial slopes of V-HDPE and R-HDPE with both organic peroxides as a function of peroxide loading. As expected, initial slopes of the Rheotens curves increased with composition of both peroxides with V-HDPE and R-HDPE. Additionally, initial slopes increase sharply beyond 0.05% of peroxide which is quite interesting. Noticeably, it increased more with 1, 3 1, 4 Bis (tert- butylperoxyisopropyl) Benzene (OP2) than dicumyl peroxide (DCP)) for concentration beyond 0.05 wt %. Change in initial slope is due to increase in peroxide composition due to higher degree of branching structure (three dimensional networks). The system showed fast relaxatation time and required lower stretching force due to lower degree of branching (<0.05 wt%). Chain mobility was restricted by more branching points at higher composition (>0.05 wt %) of peroxide. These branches align in the direction of flow and restrict the chain mobility (figure 4-25). Less mobility of chain causes more force needed to stretch polymer and thus increase in melt strength, extensional viscosity and initial slope. Sharp increase in the initial slope is observed for R-HDPE with DCP and OP2 (figure 4-24). Small concentration of carbon black as polymer–filler interaction in the R-HDPE worked together with peroxide to increase in initial slope. However, Kao et al (2002) reported that there was no improvement in the initial slope of the polypropylene-$CaCo_3$ system for all filler concentration. Thus, improvement in the initial slope for peroxide modified R-HDPE may or may not be because of small concentration of carbon black.

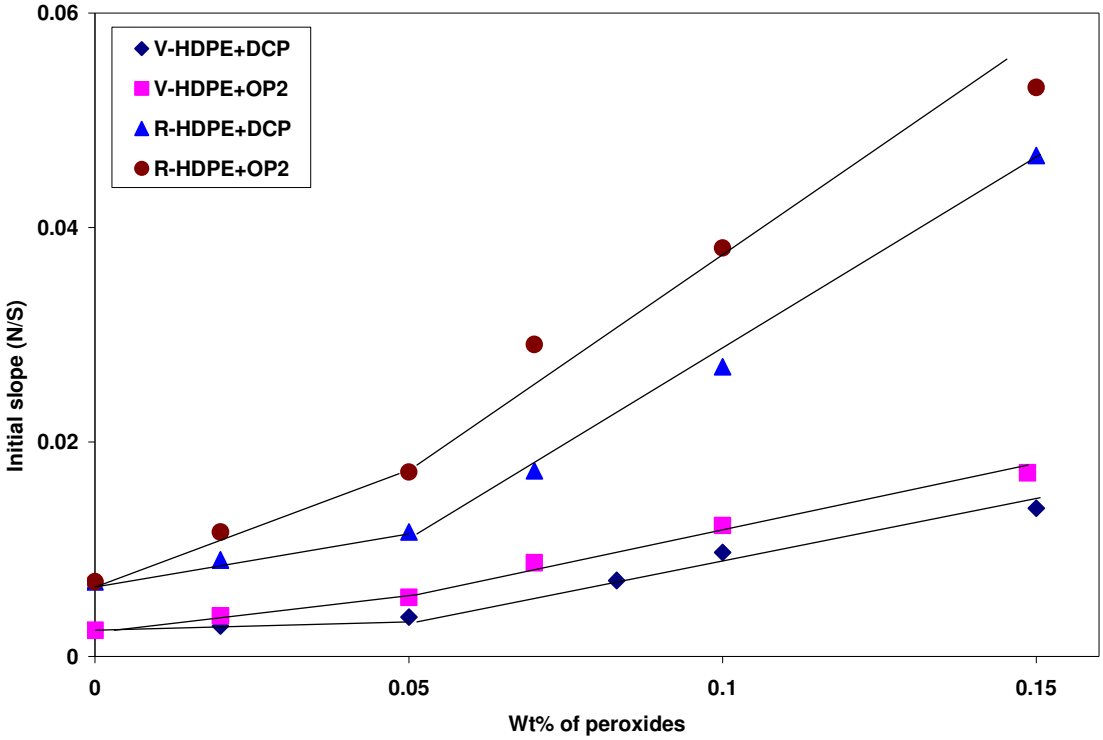
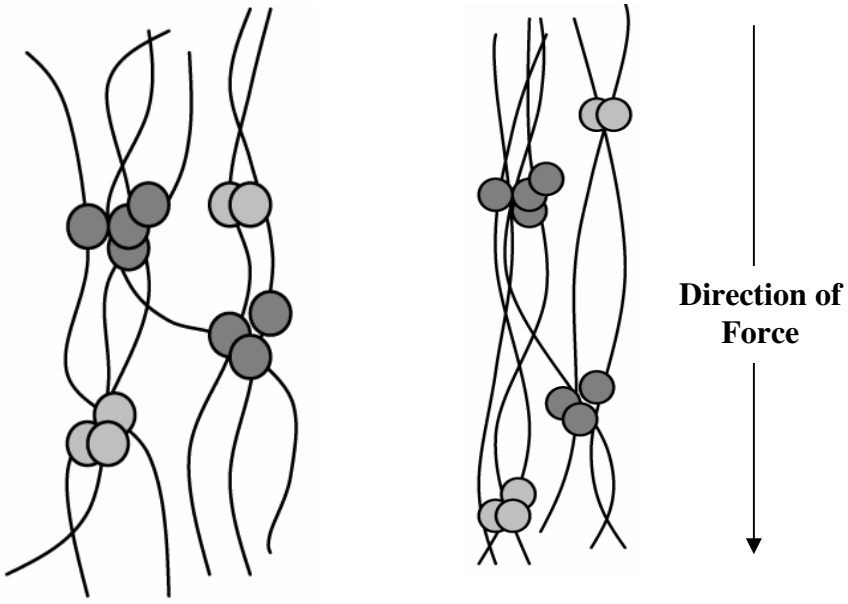


Figure 4-24 Initial slope curve of V-HDPE and R-HDPE with DCP and OP2 against Wt% of peroxide, slopes were obtained from the initial region of draw force – time Rheotens curves (not shown)



(a) (b)

Figure 4-25 Schematic presentation of alignment of branches in the direction of stretching force (a) polymer chains at rest (b) chain are in the stretching state

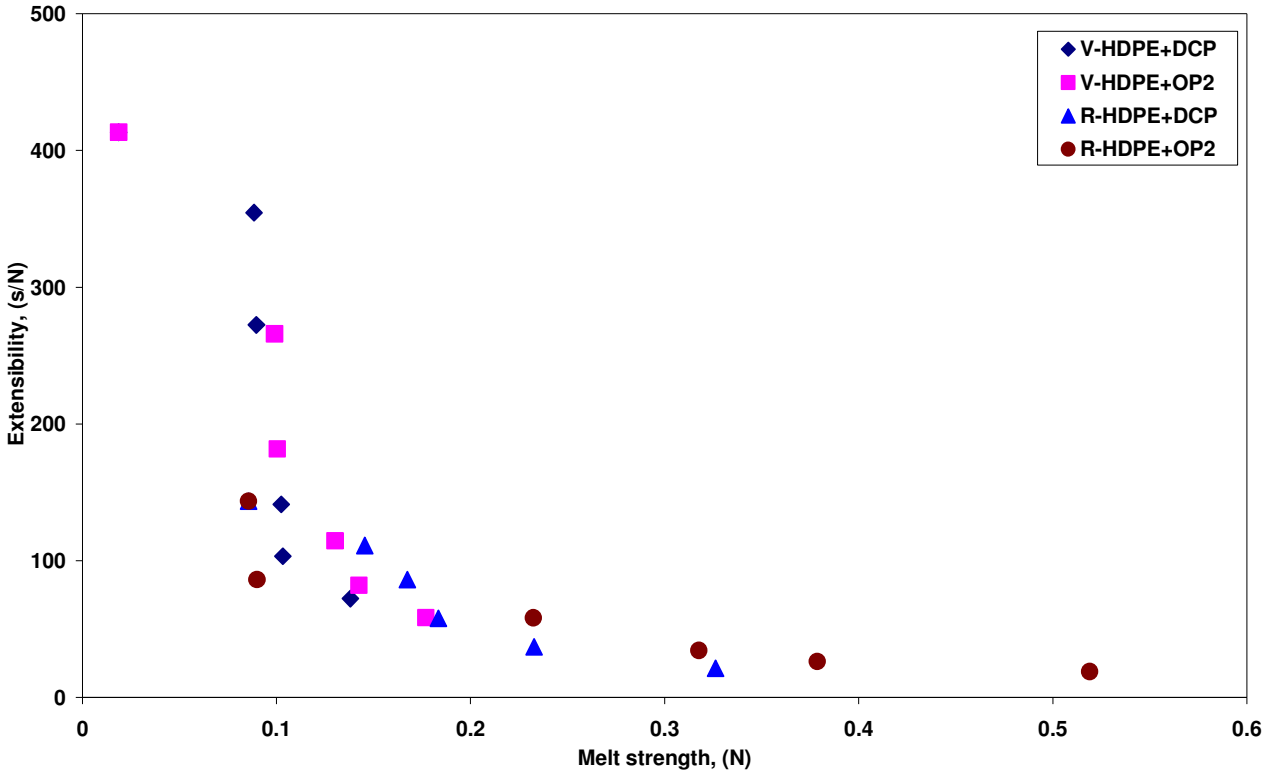


Figure 4-26 Extensibility of V-HDPE and R-HDPE with DCP and OP2

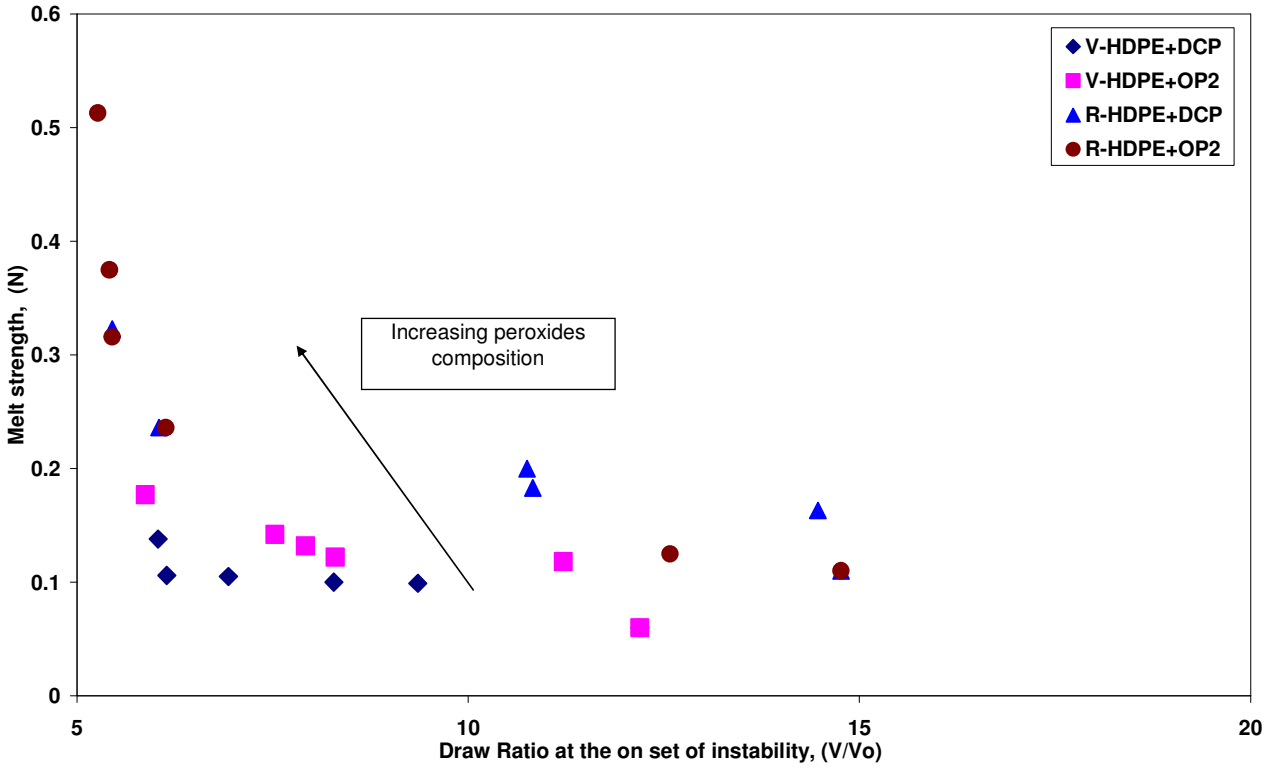


Figure 4-27 Correlation between melt strength and draw ratio at the on set of flow instability for V-HDPE with DCP and OP2

Extensibility is defined as the inverse of initial slope of draw down force-time curve and thus it has unit of time per force (s/N). It is the time required to extend the material when a unit draw force is applied. Figure 4-26 shows the extensibility plotted as a function of melt strength for virgin and recycled HDPE with both organic peroxides. It is clearly demonstrated in figure 4-26 that, strand of the modified material could not be stretched for long time as peroxide composition increased. Extended chain mechanism is the probable reason for decrease in drawability as it creates more branching points in the polymer when peroxides are reactively extruded. Organic peroxides abstract hydrogen atoms from the polymer backbone and it creates free site at which another free site can attach and make braches or entire branching network. Branching network restrict chain mobility due to crosslinks between those chains and because of it melt strength increased at the same time, drawability decreased. As shown in figure 4-27, onset of instability shifts to draw ratios as melt strength increased. It could not be said for all circumstances that, increasing melt strength cause shift in the on set of instability to lower draw ratios. However, it proves that flow instabilities occurred at lower draw ratios when entanglements occur in the polymer matrix. These flow instabilities will affect final material properties and appearance as it is related to lower nip roller velocities as well as the processing.

4.3 MODULATED DIFFERENTIAL SCANNING CALORIMETRY (MDSC)

Crystallinity refers to degree of structural order in a material. All polymeric materials are not entirely crystalline; the parts of the chains which are not in ordered state remain in amorphous state within the polymer. Most of the polymers are semi crystalline, high density polyethylene (HDPE) is also one of the semi-crystalline polymers. It is clearly observed in figures 4-32 and 4-33 **Error! Reference source not found.Error! Reference source not found.**that crystallinity and heat of fusion of the samples decreased with peroxide loading. As mentioned earlier the degree of crystallinity is calculated from ΔH_m (specific enthalpy of melting). Specific enthalpy of melting can be calculated from the area under the curve of the melting endotherm. Figures 4-28 to 4-31 show the MDSC thermographs obtained for V-HDPE and R-HDPE with DCP and OP2 respectively. As shown in figures 4-28 to 4-31, the area under the curve became smaller as peroxide loading increased, which means crystallinity decreased with increase in peroxide loading. The same behaviour of melting endotherm was observed by Shen et al (1996) when they chemically crosslinked UHMWPE (ultra high molecular weight polyethylene) with 2, 5 dimethyl-2-5bis (tert-butylperoxy)-3-hexyne. Lachtermacher and Rudin (1995b;1996a) also reported that there was decrease in melting peak heights of modified LDPE, LLDPE and HDPE. Organic peroxides are used to enhance extended mechanism in the liner polymers. Decomposed free radicals of the peroxide abstract hydrogen atoms from polymer macromolecule and finally carbon–carbon atoms combines in the alkyl radicals to produce cross links. Branched or crosslinked HDPE samples have more branching points and these points suppress crystal growth and produce imperfect crystals, resulting in the decrease in crystallinity (Shen et al., 1996). Moreover, decrease in crystallinity is attributed to the inhibition of crystal growth and decrease crystal size by peroxide induced cross links (Shen et al., 1996).

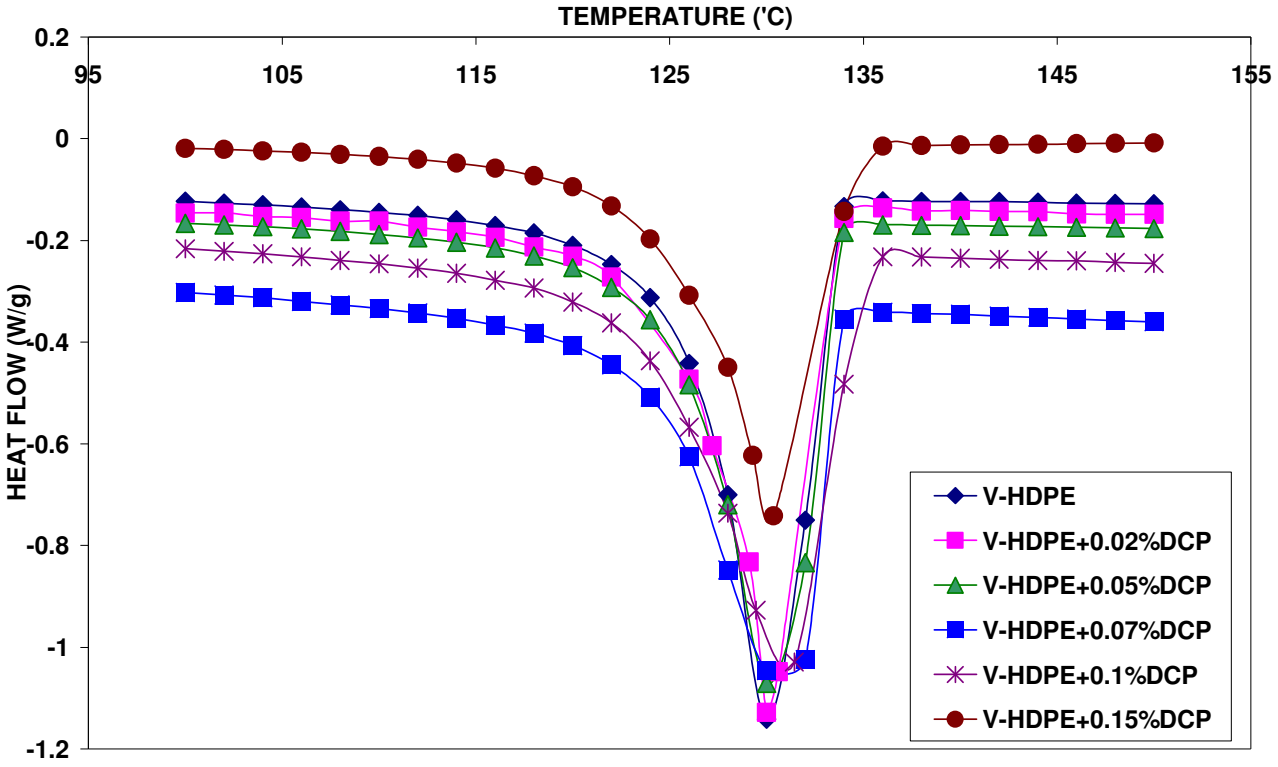


Figure 4-28 MDSC thermograph of V-HDPE with DCP at second heating cycle @ 2° C/Min

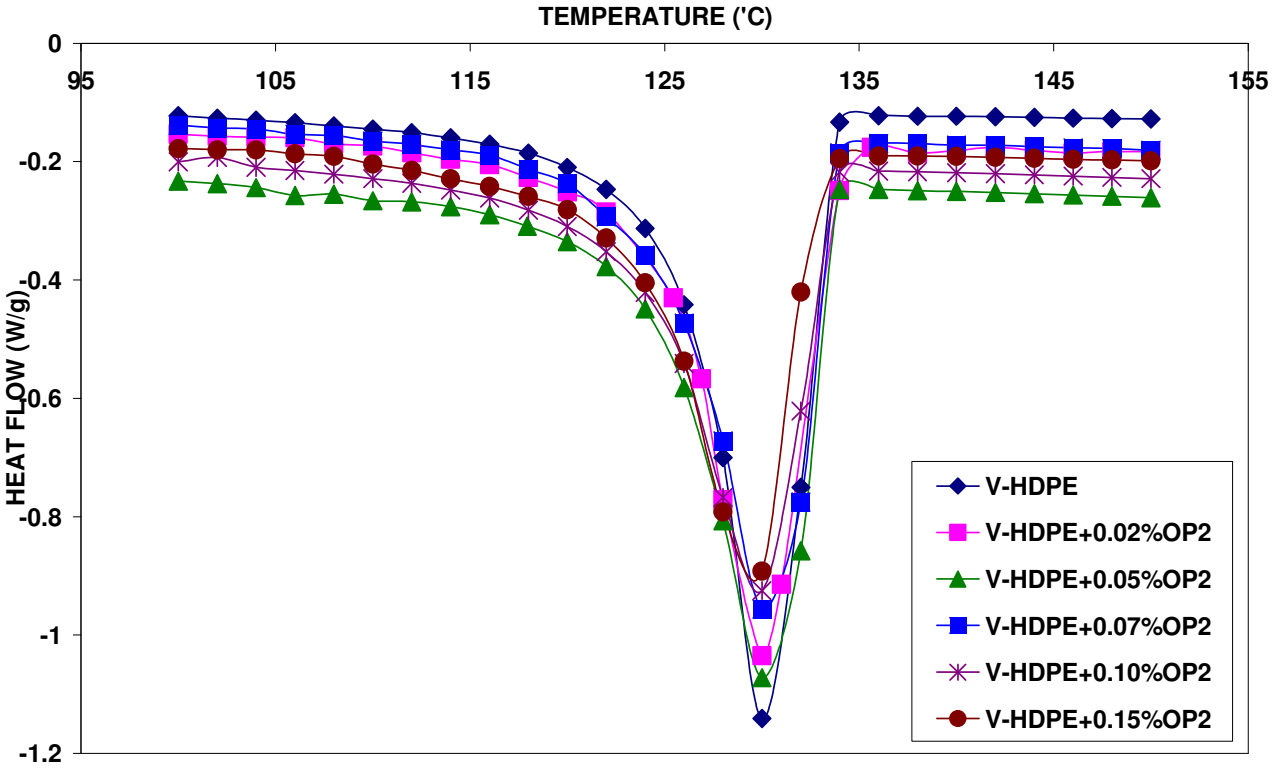


Figure 4-29 MDSC thermograph of V-HDPE with OP2 second heating cycle @ 2° C/Min

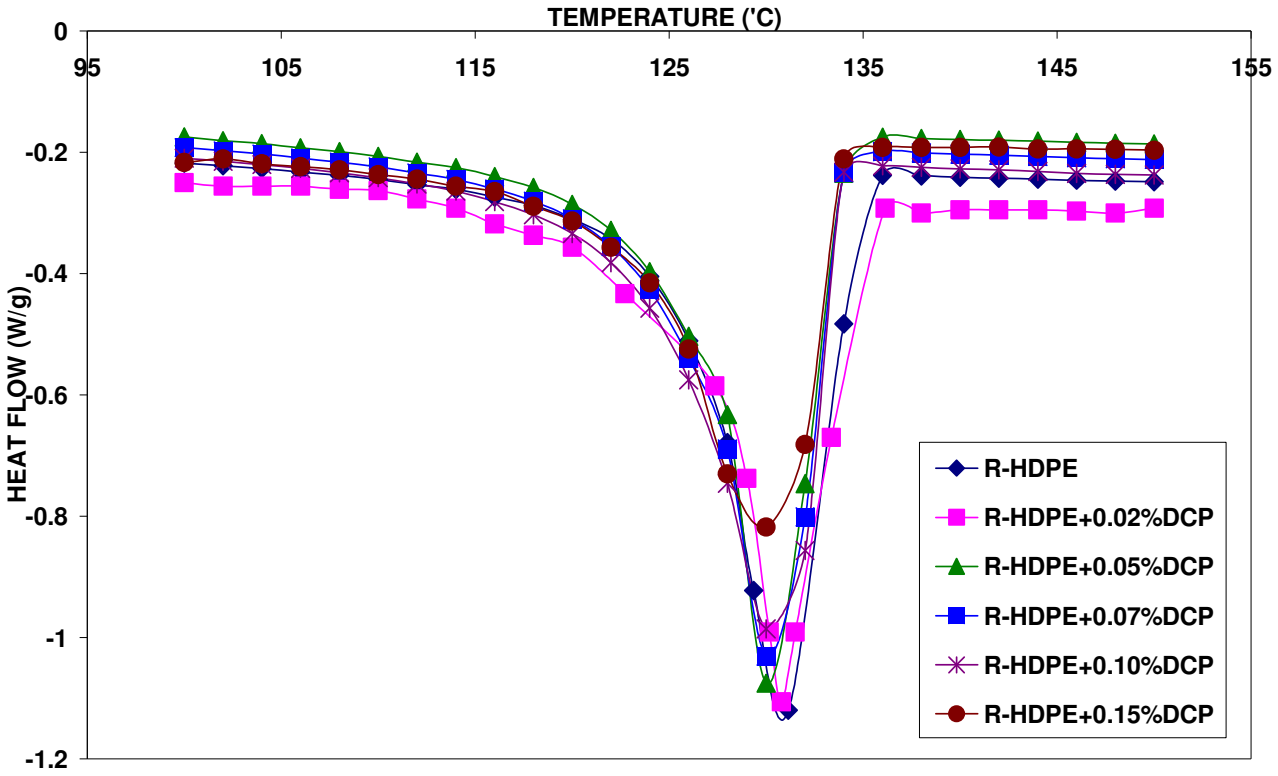


Figure 4-30 MDSC thermograph of R-HDPE with DCP at second heating cycle @ 2° C/Min

Melting point temperature remained almost unchanged with peroxide loading**Error! Reference source not found.Error! Reference source not found.**. The possible reason for the observed small changes in the melting point temperature is related to the lamellae thickness of the polymer chains. When polymer is heated to its melting point, the lamellae thicken and give rise to its melting behaviour. Conversely, peroxide crosslinked network hinders re-crystallisation and crystal thickening is restrained by crosslinking (Salovey and Bassett, 1964). Moreover, when partially crosslinked polyolefin is heated above its melting point, the macromolecular chains are still held together by the three dimensional network. All applied forces are converted in elastic deformation and broadening the processing window. Flory (1955) suggested that the melting point demoralization of a peroxide treated samples was due to the reduction in the concentration of segments of a length suitable for crystallization.

Figures 4-30 and 4-31 show the MDSC endotherm for recycle HDPE (carbonblack filled) with both peroxides respectively. It seems that degree of crystallinity decreased as peroxide content increased. It was observed that there is no effect of carbon black filler on the degree of crystallinity. Decrease in the degree of crystallinity is purely from organic peroxide crosslinking or extended chain mechanism. According to Tang et al

(1994) there is no practical effect of carbon black filler on the degree of crystallinity. In addition, free radical reactions between filler and polymer matrix may not present because free radical of carbon black is very stable (Rånby and Rabek, 1977). Cheshkov et al (1991) also observed that addition of the calcium phosphate filler into nylon-6 had little or no influence on the crystallinity of the system.

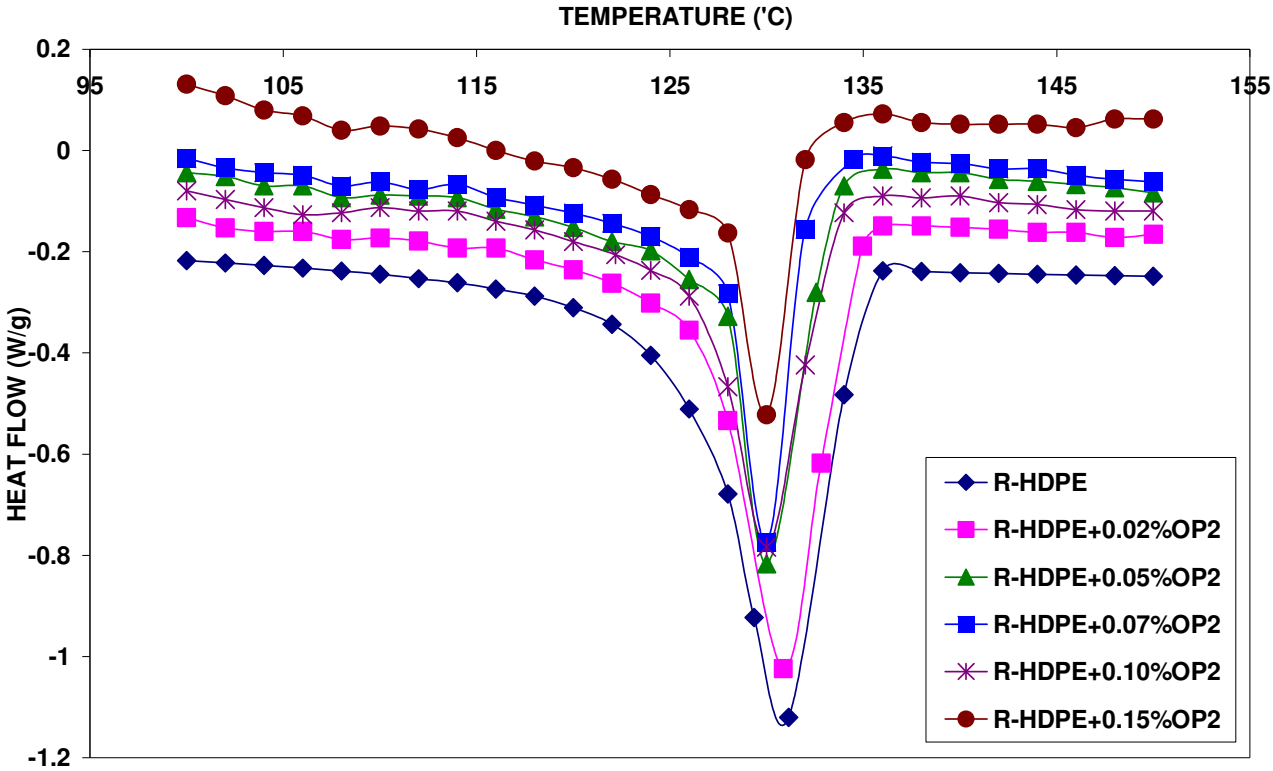


Figure 4-31 MDSC thermograph of R-HDPE with OP2 at second heating cycle @ 2° C/Min

Heat of fusion refers to the amount of heat absorbed or evolved to change the state of material from solid to liquid or vice versa. As shown in figure 4-33**Error! Reference source not found.Error! Reference source not found.**, heat of fusion decreased with peroxide loading. However, linear relationship was observed between crystallinity and heat of fusion because both are purely based on the melting endotherm. Khonakdar et al (2003) reported the same behaviour of heat of fusion (ΔH_m) while investigating the crosslinking of HDPE with di-tert butyl cumyl peroxide (BCUP). Heat of fusion decreased with increase in the degree of crosslinking. This decrease was not caused by reduction in the crystalline portion but by an increase in the enthalpy of the crystal surface (Chodák, 1995).

Table 4-4 Temperature ranges of three transitions observed in DMA analysis

Transitions	Temperature range (°C)
α	20 to 70
β	-45 to 20
γ	-150 to -110

As cited in literature, three peaks named α, β and γ transitions are observed in dynamic mechanical analysis (DMA) of polyolefins followed by melting. Temperature range for all three transitions is given in table 4-4**Error! Reference source not found.**. T_g for HDPE is also in the same rage of γ transition. Khonakdar et al (2003) further reported that, an increase in the degree of crosslinking results in a decrease in temperature of γ transition which causes a decrease in crystallinity, thus enhancing the molecular motion in the amorphous region resulting in an increase in the free volume and hence lowers down the T_g. T_g refers to the temperature above which non-covalent bonds between the polymer chains become weak in comparison to thermal motion, and the polymer becomes rubbery and capable of elastic or plastic deformation without fracture. This behavior is utilized in the application of plastics. Decrease in T_g with crosslinking makes plastic more elastic and broaden the processing window. Thus it can be concluded that, crosslinking or branching mechanism is responsible for decrease in crystallinity as observed and also lowers down the T_g.

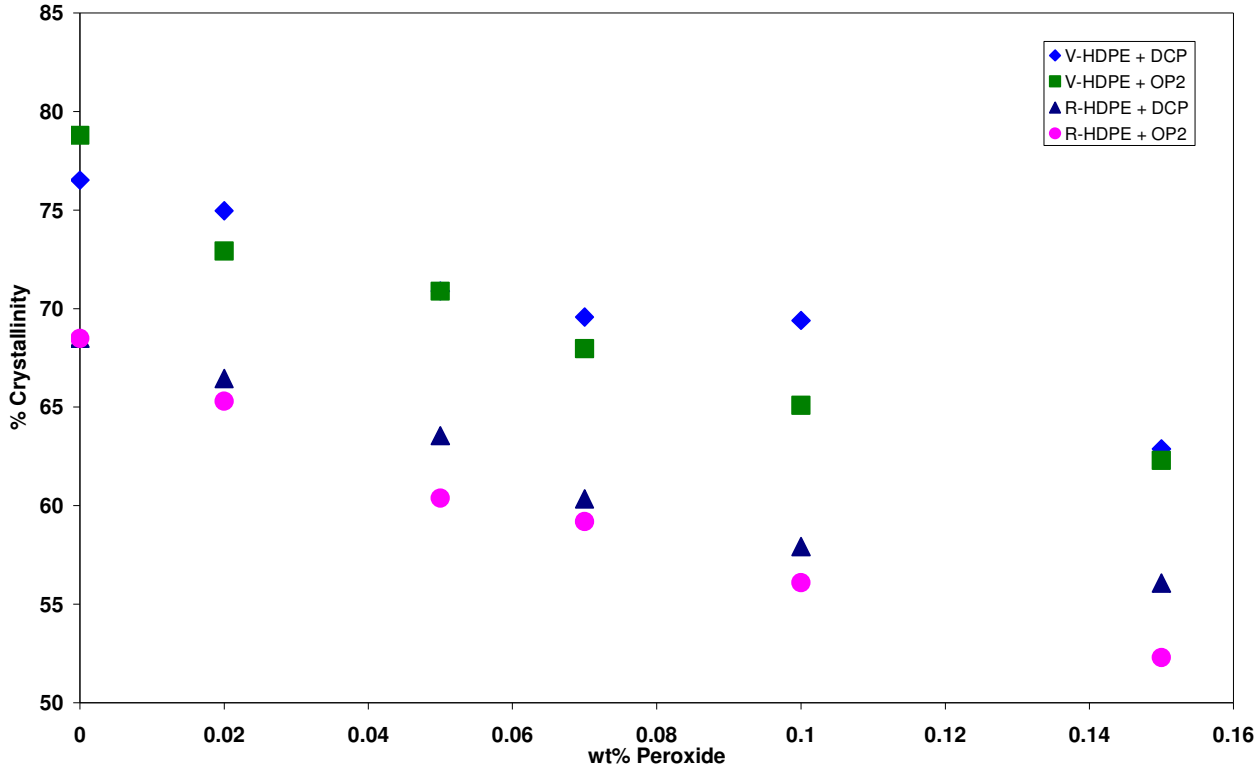


Figure 4-32 %crystallinity of modified and unmodified V-HDPE and R-HDPE as a function of peroxide concentration (wt%)

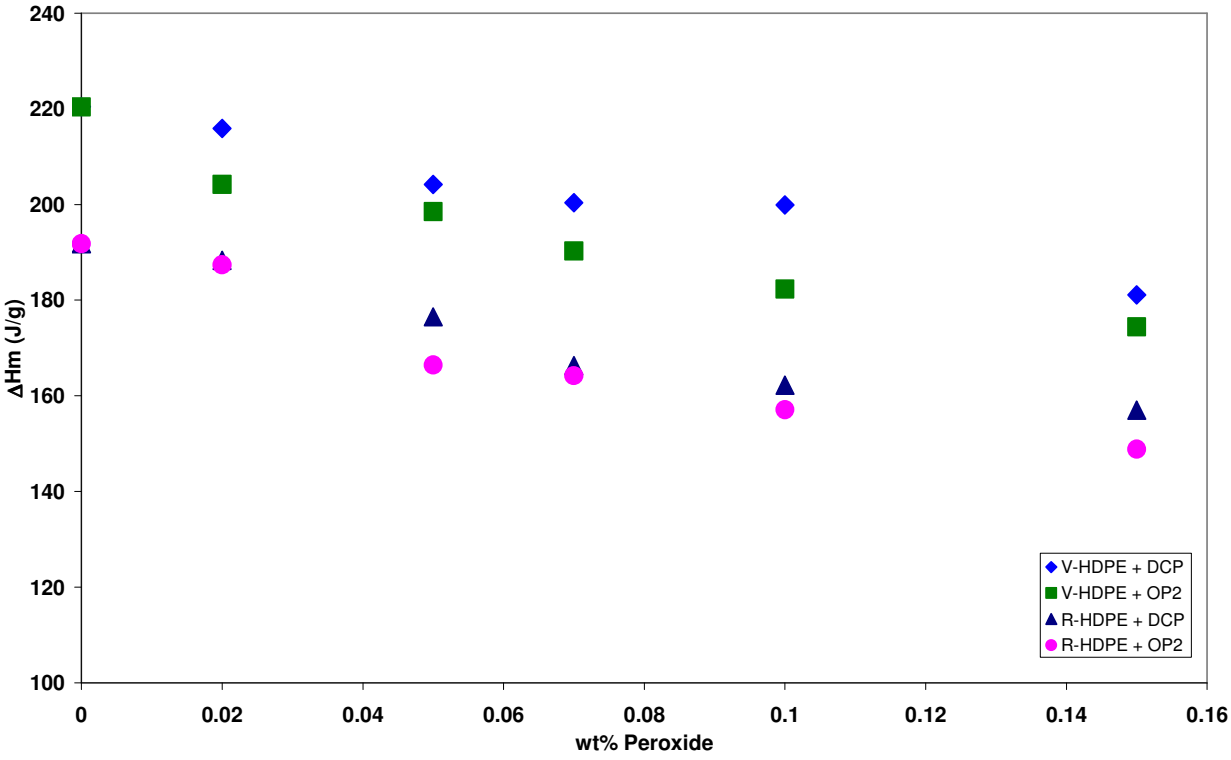


Figure 4-33 Heat of fusion of modified and unmodified V-HDPE and R-HDPE as a function of peroxide concentration (wt%)

4.4 GEL PERMEATION CHROMATOGRAPHY (GPC)

The influence of long chain branching (LCB) on the properties of polyolefins (Gotsis et al., 2004a, Gotsis et al., 2004b, Münstedt et al., 1998, Santamaria, 1985, Liu et al., 2002) and particularly for high density polyethylene has been extensively studied (Perez et al., 2002). Gel permeation chromatography or size exclusion chromatography were employed to evaluate molecular weight, molecular weight distribution and long chain branching (LCB). Weight average molecular weight (Mw), number average molecular weight (Mn), polydispersity index (PI) and molecular weight distribution (MWD) are necessary to explain molecular characterisation of the modified and unmodified HDPEs.

Table 4-5 lists the molecular parameters obtained by GPC of virgin and recycled HDPE samples before and after peroxide modification using different compositions of both peroxides. It can be seen that al1 the molecular weight averages for modified virgin and recycled HDPE are much higher than those of the unmodified samples used for experiment in the present study. As expected, the molecular weight averages of modified V-HDPE and R-HDPE increased with increase in the peroxide concentrations. For the better explanation of these observations, the actual molecular weight distribution (MWD) curves for all of these modified and unmodified virgin and recycled HDPE are shown in figure 4-34 and figures A-12 to A-14 (appendix). It can be observed that with increasing peroxide concentration, the distribution is progressively moved towards higher molecular weight, while the change in the high molecular weight end seems relatively small. This is fully in agreement with previous works (Perez et al., 2002, Wood-Adams et al., 2000). Molecular weight distribution shift towards high molecular weight end and also peak height decreased with peroxide compositions. Decomposed products attack on the polymer chains and free sites were created by hydrogen abstraction. These polymer chains combine together to make long chain branching mechanism due to the instability of these chains. Long chains contain high molecular weights and these high molecular weights fragments cause MWD shift towards higher molecular weight ends in the distribution.

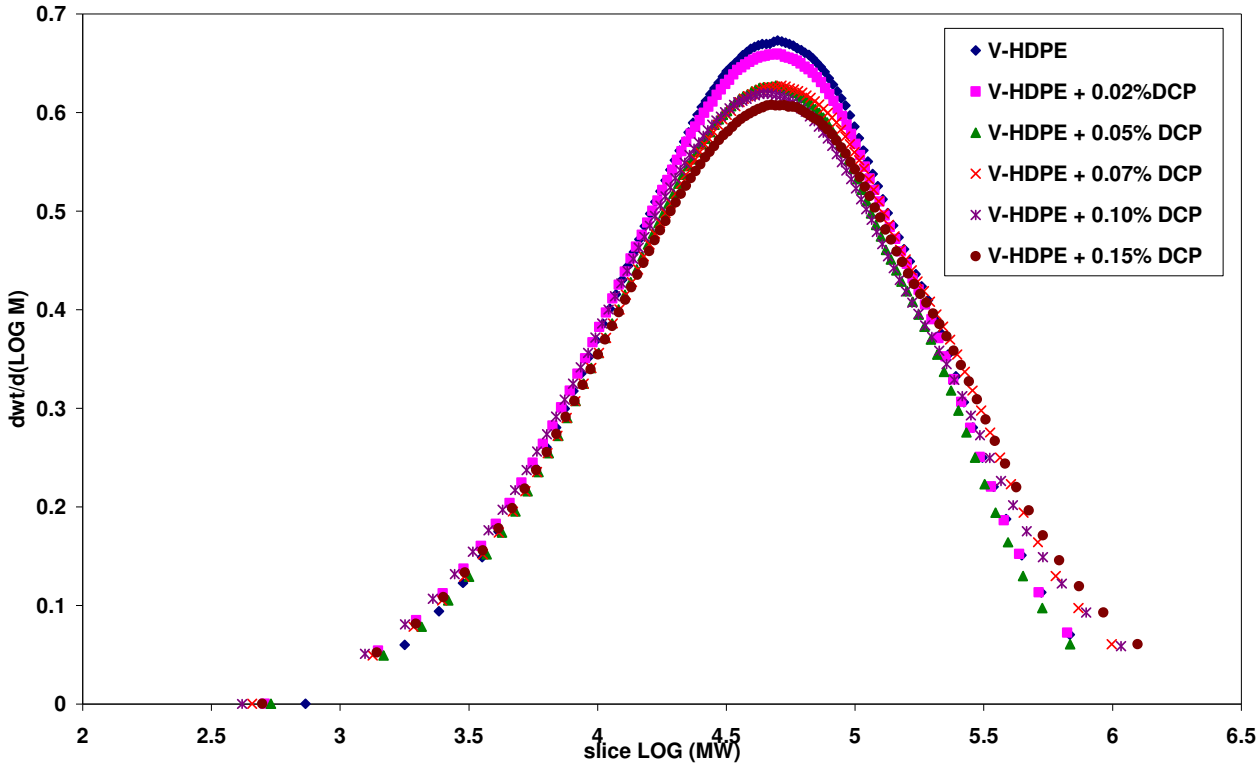


Figure 4-34 Molecular weight distribution (MWD) for V-HDPE + DCP

Table 4-5 Molecular parameters of peroxide modified and unmodified V-HDPE and R-HDPE

Wt% Peroxide	V-HDPE + DCP				
	Mw	Mn	PI	Intrinsic Viscosity	g' (Branching Index)
0	91719	16837	5.447467	1.69	1
0.02	92302	17908	5.154233	1.68	0.99408284
0.05	92955	17283	5.378407	1.67	0.98816568
0.07	113808	21342	5.332584	1.62	0.958579882
0.1	114507	22091	5.183423	1.72	1.017751479
0.15	129280	23564	5.486335	1.63	0.964497041
Wt% Peroxide	**R-HDPE + DCP**				
	Mw	Mn	PI	Intrinsic Viscosity	g' (Branching Index)
0	89814	39836	2.254594	1.29	1
0.02	91254	39925	2.285636	1.28	0.992248062
0.05	97270	41152	2.363676	1.28	0.992248062
0.07	115365	41958	2.749535	1.26	0.976744186
0.1	118429	43954	2.694385	1.25	0.968992248
0.15	132856	44729	2.970243	1.26	0.976744186

Wt% Peroxide	V-HDPE + OP2				
	Mw	Mn	PI	Intrinsic Viscosity	g' (Branching Index)
0	91719	16837	5.447467	1.69	1
0.02	116830	18555	6.296416	1.65	0.976331361
0.05	122556	17639	6.948013	1.63	0.964497041
0.07	124558	18842	6.610657	1.69	1
0.1	127686	19254	6.631661	1.6	0.946745562
0.15	130437	21564	6.048831	1.6	0.946745562
Wt% Peroxide	**R-HDPE + OP2**				
	Mw	Mn	PI	Intrinsic Viscosity	g' (Branching Index)
0	89814	39836	2.254594	1.29	1
0.02	121549	41486	2.92988	1.27	0.984496124
0.05	123476	42869	2.88031	1.26	0.976744186
0.07	130256	43698	2.980823	1.25	0.968992248
0.1	132548	43987	3.013345	1.23	0.953488372
0.15	135176	44569	3.03296	1.23	0.953488372

As shown in figures A-12 to A-13 (appendix), more shifts are observed in MWD towards high molecular weight ends with V-HDPE and R-HDPE modified by OP2 as compared to DCP (figures 4-34 and A-13 (appendix)). Higher crosslinking efficiency of OP2 due to the high active oxygen content is the possible reason for these more shifts.

The g' (branching index) is also one of the important factors to compare long chain branching among modified and unmodified samples. It can be calculated at each slice across the molecular weight distribution and the average value of g' for the whole polymer can be obtained. Decrease in g' indicates branching as shown in table 4-5.

The Mark-Houwink equation for the linear polymers in the GPC solvent relates intrinsic viscosity to the viscosity average molecular weight (Mv).

$$[\eta] = KM_v^{\alpha} \qquad \textbf{(4.1)}$$

Where,

[η] = Intrinsic viscosity of a polymer for a given conditions

Mv = Mw = viscosity-average molecular weight (for monodisperse polymers)

K and α are the Mark-Houwink constants

Intrinsic viscosity is defined as the capability of a polymer in a solution to enhance viscosity of the solution. Log-log plot of [η] against molecular weight can be generated that cover the entire distribution of molecular weights for any given sample. Theoretically, for a linear polymer the viscosity law plot (log [η] versus log M) is linear across the molecular weight distribution with an intercept equal to log K and a slope equal to a. Such relationships are called Mark-Houwink plot. This plot can be used to describe the molecular structure of the polymer qualitatively. However, this relationship is not applicable for entire molecular weight distribution. Figure 4-35 and figures A-15 to A-17 (appendix) shows the Mark-Houwink plots for V-HDPE and R-HDPE modified by DCP and OP2 respectively. Unmodified HDPE's was taken as linear polymer for this study and all the modified samples were plotted with reference to the unmodified HDPE's. All the modified randomly branched polymer samples exhibit typical shape as exhibited by Bruno and Walter (1949). They intersect the linear sample curve at lower molecular weight and exhibit largest deviation at higher molecular weight region of the distribution. As seen in the figure 4-35 and figures A-15 to A-17 (appendix), the same

kind of deviation can be noticed as molecular weight and degree of branching increased. This deviation is more experienced in OP2 modified samples due to higher formation of branched structure. Other noticeable feature in these figures (figure 4-35 and figures A-15 to A-17 (appendix)) is that at low frequency, LCB extent appears within the relatively low molecular weight region. Although chain branching may also occur as a result of recombination reactions. Other factors may also cause the appearance of LCB in this region, such as

a) The Mark-Houwink relationship may not apply across the whole molecular weight range.
b) Insensitivity of the molecular weight detectors towards low molecular weight species.
c) The experimental noise in the detector signals

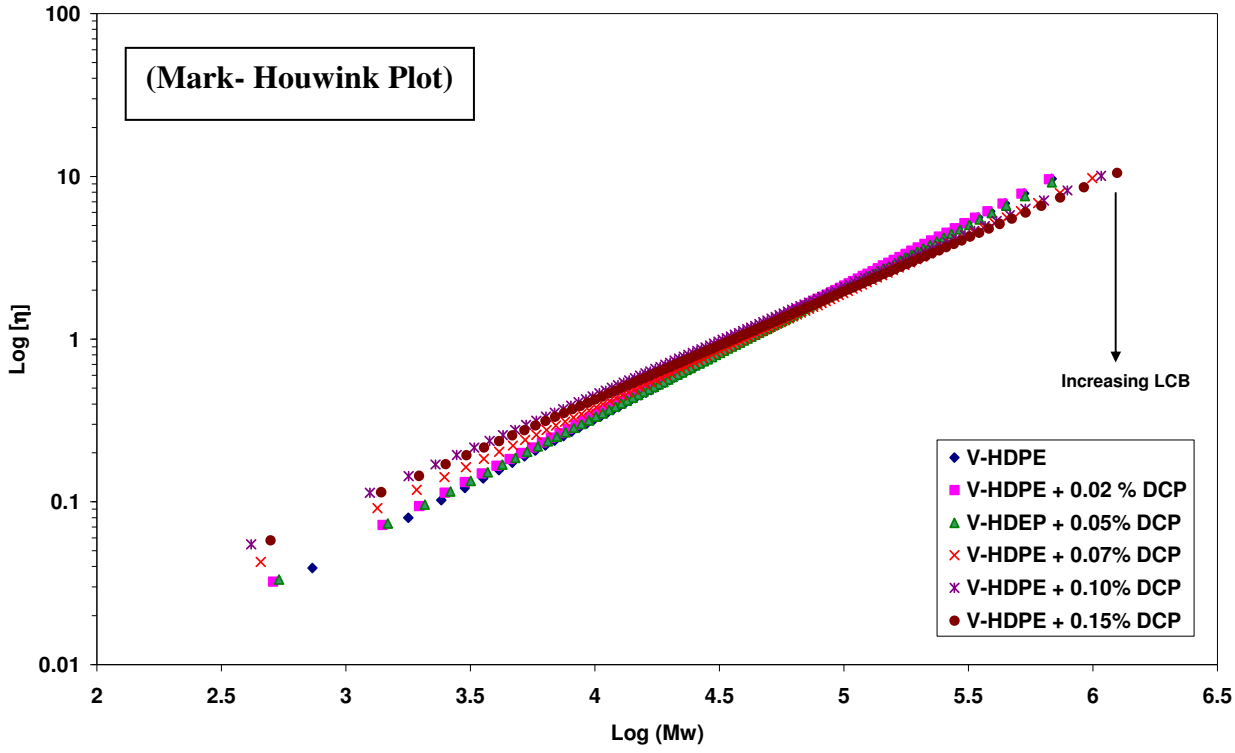


Figure 4-35 Intrinsic viscosity as a function of Molecular weight for V-HDPE+DCP

4.4.1. LCB-Rheology Relations

Effects of long chain branching on rheological behaviour of peroxide modified materials have significant role in the characterisation of these materials. Degree of branching, its structure and branching level all affects the rheological behaviour in different ways. This relationship is also affected by variation in molecular weight and its distributions.

It is generally accepted that, molecular structures such as such as molecular weight (Mw), molecular weight distribution (MWD) and molecular orientation like long chain branching possessed by different materials have significant effect on the different rheological properties.

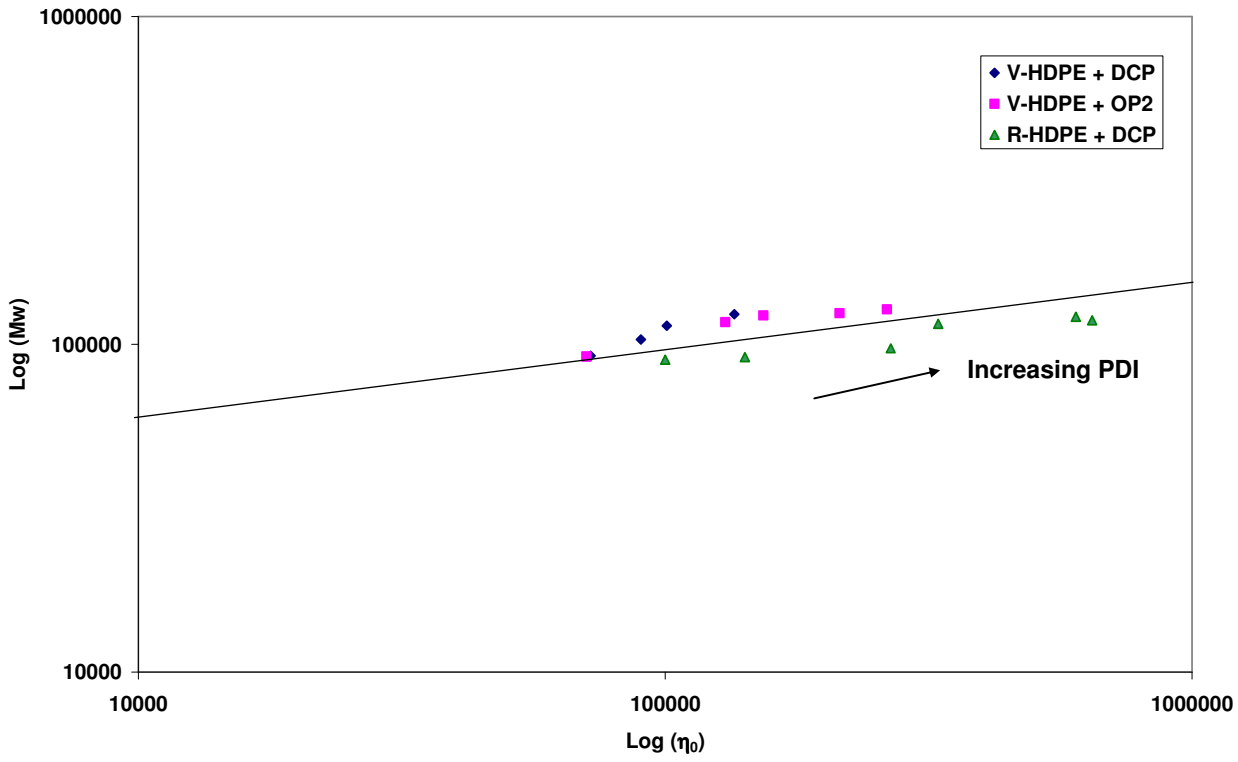


Figure 4-36 Effect of long chain branching on zero shear viscosity as a function of molecular weight (Mw) and polydispersity index

Figure 4-36 shows the effect of polydispersity index on the zero shear viscosity. Zero shear viscosity was plotted against weight average molecular weight on the log-log plot. Increase in molecular weight results in exponential increase in zero shear viscosity (Wood-Adams et al., 2000). Raju et al (1979) also reported exponential relational

relationalship between zero shear viscosity and chain molecular weight Carella et al (1986) and Fetters et al (1993) confirmed this finding. Better enhancements were observed for OP2 modified samples. It was clearly observed from the figure 4-36 that, polydispersity index has significant effect on zero shear viscosity. Zero shear viscosity enhancement was observed by Janzen and Colby (1999) with increase in degree of branching when modification was done by even low level of peroxide. Moreover, the zero shear viscosities of the blends were not less than those of the pure components. The authors interpreted this to mean that the viscosity enhancement does not depend on the interaction between two branched molecules but rather on the interaction of a branched chain with other entangled chains.

4.5 MECHANICAL CHARACTERISATION

Tensile behaviour of peroxide modified virgin and recycled HDPE were measured by Instron Universal Testing Machine (model no.-4467. Instron Corporation, England) according to ASTM standards D638-01 (ASTM D638-01, 2001). Compression moulded plaques (@ 190°C and 120 kN) were cut into dumbbell-shaped specimens (type-1) according to ASTM D638-01 and all measurements were done at 50mm/min crosshead speed. Tensile strength, Young's modulus and % elongation were measured and these results are discussed in the following section.

4.4.2. Tensile Strength

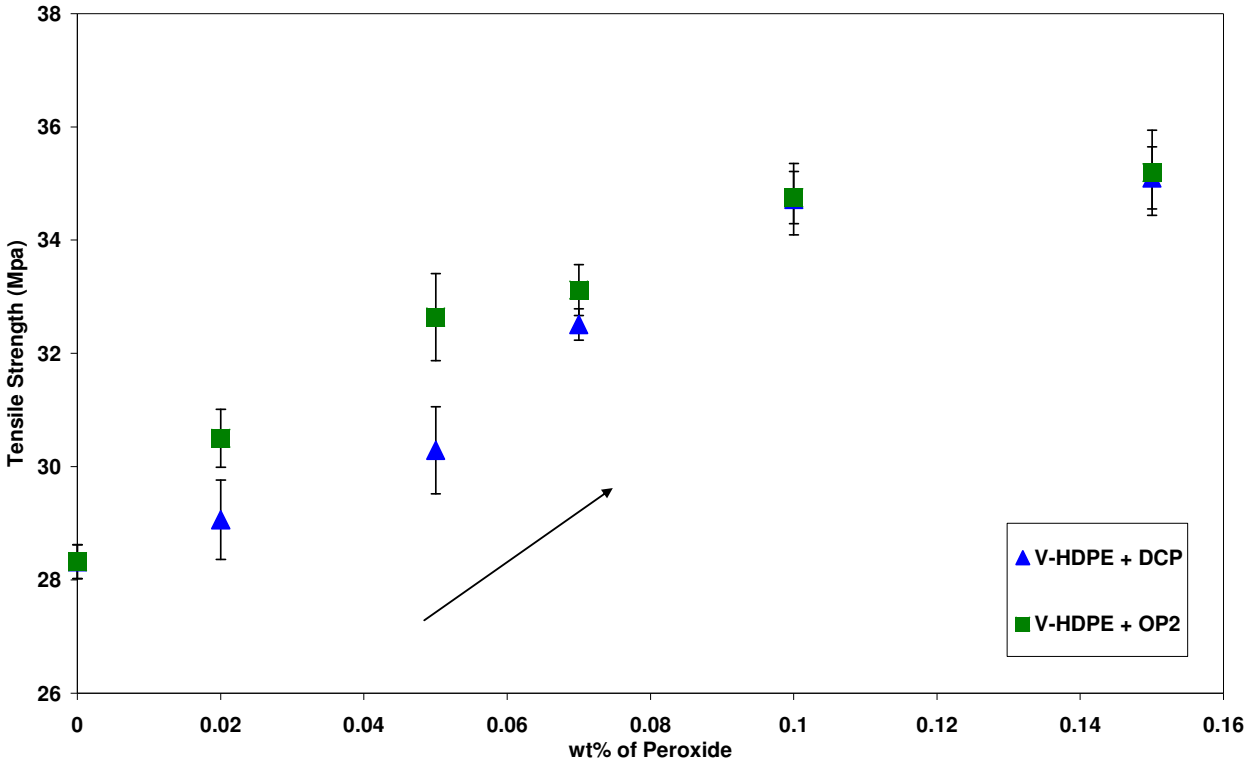


Figure 4-37 Tensile strength of V-HDPE with both peroxides

Figures 4-37 and 4-38 show tensile strength for V-HDPE and R-HDPE modified by both peroxides respectively. It can be seen that enhancement in tensile strength was found with all modified materials. Tensile strength increased almost linearly with increasing compositions of peroxides. However, highest compositions of both peroxides showed non-linear behaviour of increment in tensile strength. Conversely, all compositions of R-HDPE modified by both peroxides observed almost linear increase

with peroxide compositions. Tensile behaviour has direct relation with crystalline structure and morphology of the polymer (Chodák, 1995). As expected, peroxides form extended chain mechanism via chain linking or crosslinking process, since more stress was required to break the branched sample due the alignment of all chains in the direction of stress and hence tensile strength is higher in case of peroxide modified samples as compared to the un-modified samples. In addition, tensile strength of un-modified recycled samples was slightly lower than the virgin unmodified counterparts. Small amounts of carbon black played its role in this decrement. Decrease in tensile strength with filler was reported by Atikler et al (2006).

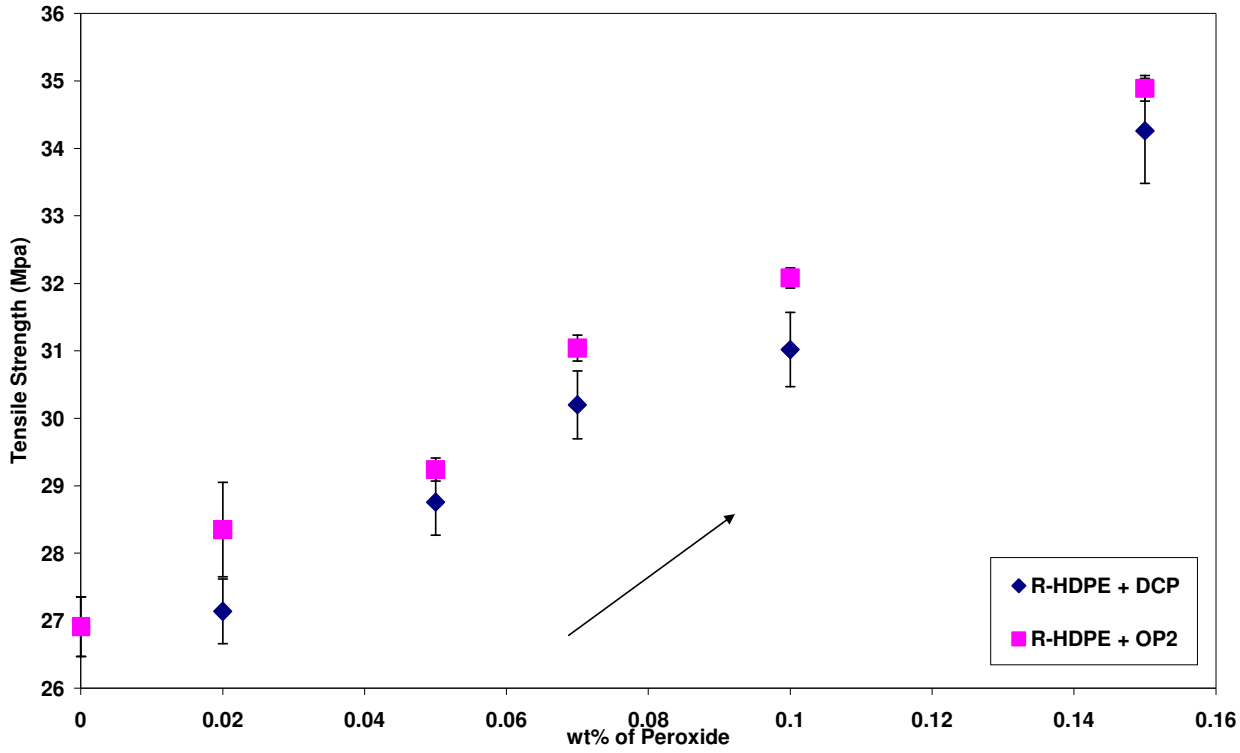


Figure 4-38 Tensile strength of R-HDPE with both peroxides

Introduction of free radical initiator (organic peroxide) causes branching mechanism within the polymer backbone. This process occurs at high temperature as it is necessary to decompose the peroxide. This branching mechanism causes significant change in the morphology and crystalline structure of the modified polymer. Moreover, in semi-crystalline and high molecular weight polymer, it is very difficult to pull out the long chain molecules from the entanglements and these long chain molecules similarly behaves like tie molecules in crystalline polymer and give comparable improvement in mechanical behaviour. Parez et al (2003) reported enhancement in tensile strength with

increase in molecular weight of the linear HDPEs modified by 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane. They further noted the role of crystallinity in the improvement of tensile behaviour of the peroxide modified linear HDPEs.

4.4.3. Young's Modulus

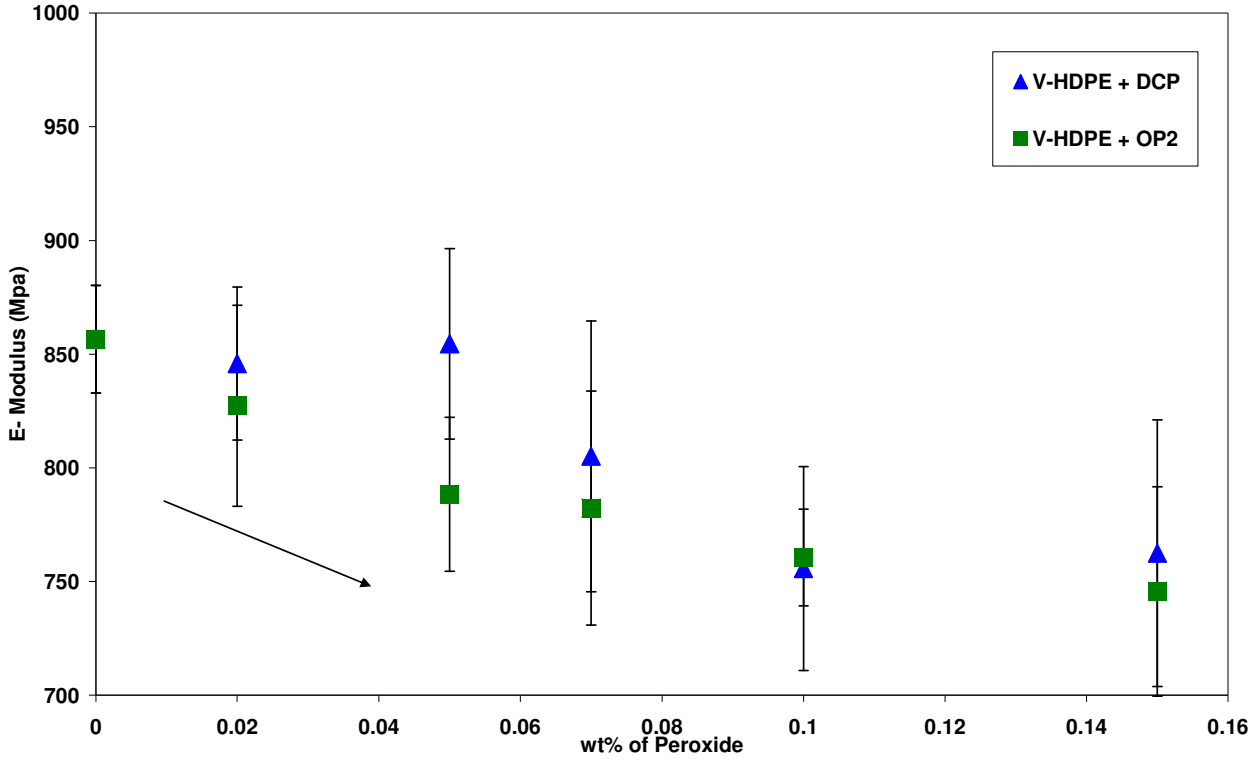


Figure 4-39 Young's modulus of V-HDPE with both peroxides

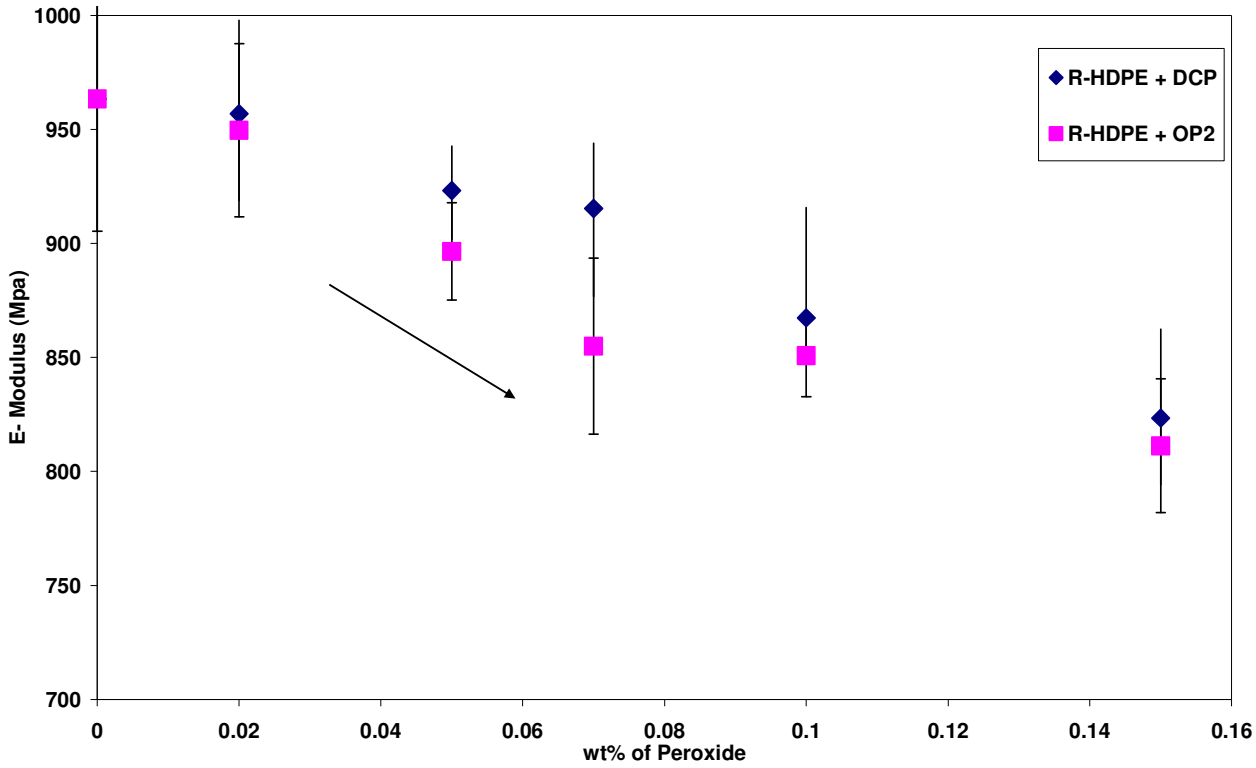


Figure 4-40 Young's modulus of R-HDPE with both peroxides

Figures 4-39 and 4-40 show the Young's modulus of V-HDPE and R-HDPE modified by both DCP and OP2 respectively. As shown in figure 4-39 Young's modulus decreased with peroxide concentration monotonically. Young's modulus was calculated from slope of the stress-strain curve form the transition region where the linear region just finished and just before the commencement of non-linear region. As peroxide composition increased modified materials lost some of their elasticity which was apparent from the lower values of Young's modulus. Figure 4-40 also showed decrease in modulus with increase in peroxide concentration. However, higher values of modulus were obtained for un-modified and modified recycled material because of the filler content (compared to the corresponding un-modified and modified virgin materials). Moreover, long chain branched molecules required more time to relax and thus relaxation spectrum is broad in this case as discussed earlier in the shear rheology section (4.1.2). This observation is also correlated to lamellar thickness as noted by Al-Hussein et al (2001) who observed that the relaxation magnitude is inversely proportional to the lamellar thickness.

Peroxide modified samples considered as consisting of crystalline lamellae held together by branched chains and separated by an amorphous phase. Crystalline phase decreased due to branching. When these peroxide modified materials are stressed, first the deformation occurs at the crystalline lamellae and amorphous layer level. Due to the presence of ordered structure, Young's modulus increased initially when stretched but decreased at the interface of crystalline and amorphous phase. Branched samples have lower crystallinity as compared to linear sample so lower Young's modulus values were observed. Further, Lu et al (2000) reported structure property relation relationship of LLDPE blown film. The authors further noted that the Young's modulus of semicrystalline polymers is governed by crystallinity, crystalline and amorphous phase orientation.

4.4.4. % Elongation

Figure 4-41 shows the % elongation of the unmodified and modified V-HDPE and R-HDPE with DCP and OP2. It was found that % elongation decreased with all peroxide modified samples. Kim and Kim (1993b) reported decrease in % elongation with peroxide modification. Conversely, Azizi and Ghasemi (2004b) reported that, elongation at break enhanced in PP modified by DCP. However, impact strength is the property which enhanced most with peroxide modification. Higher deviations were observed in the % elongation of the all modified materials. Branched polymers have tendency to be aligned in the direction of flow but at the same time slow relaxation behaviour reduce its capability during tensile testing. Modified samples had higher tensile strength but breakage of the samples was observed at lesser elongation with peroxide composition increment.

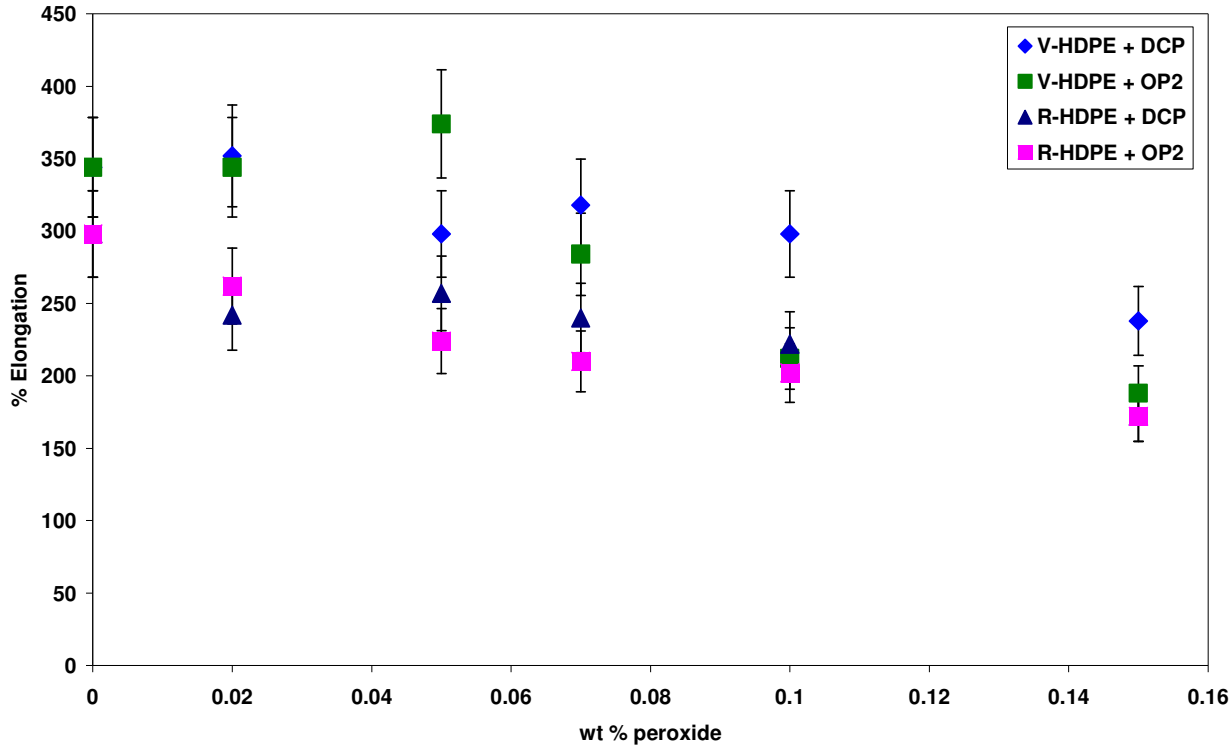


Figure 4-41 % Elongation for V-HDPE and R-HDPE with both peroxides

4.6 ENVIRONMENT STRESS CRACKING RESISTANT (ESCR)

Organic peroxide modified and unmodified materials were tested for its resistance to stress cracking. This test were carried out according to the ASTM D1693-01 (ASTM D1693-01, 2001) and results were recorded in terms of f_{50} (time for 50% of the specimens to fail). Ten specimens were used for this test and f_{50} was recorded when at least five samples failed (observed crack growth). Routine inspection was done every 2 hours after the first crack growth was observed in any specimen. Notched specimens, a strong surfactant and constant high temperature were used to speed up the effects of environmental conditions the polymers would encounter in service.

2 mm thick plaques of the samples were prepared by compression moulding at 190 °C and 120 kN (20,000 lbs). Ten specimens of each sample were notched; placed in the specimen holders and immersed in a surfactant solution of 10 vol% Igepal CO-630 at 50 °C. The specimens were checked at intervals manually and the time for at least five of out of ten specimens to fail, f_{50} was recorded.

Figure 4-42 shows the failure time of the V-HDPE and R-HDPE modified by DCP and OP2. As shown in the figure 4-42, failure time of at least five samples out of ten (50%) increased with peroxide modification. For example, ten specimens of virgin HDPE were placed in testing condition and at regular interval it was observed for initial crack growth and further growth in this crack. When initial crack and further growth in this crack was observed for any five specimens out of ten then this reading was recorded for that particular sample. Some authors (Nielsen and Landel, 1994, Lachtermacher and Rudin, 1995a, Lachtermacher and Rudin, 1995b, Lachtermacher and Rudin, 1996b, Kim and Yang, 1999, Perez et al., 2002) reported that even the small molecules in the polymer structure of the polymer produce significant changes in the melt rheological properties. Moreover, in one long chain branch every ten molecules are enough for enhancement of polymer melt viscosity, tensile strength and resistance against environment stress cracking. These significant changes include slow cracks growth of modified samples attributed to degree of branching and its effect on crystal structure, lamellar thickness and number of tie molecules (Lustiger and Markham, 1983).

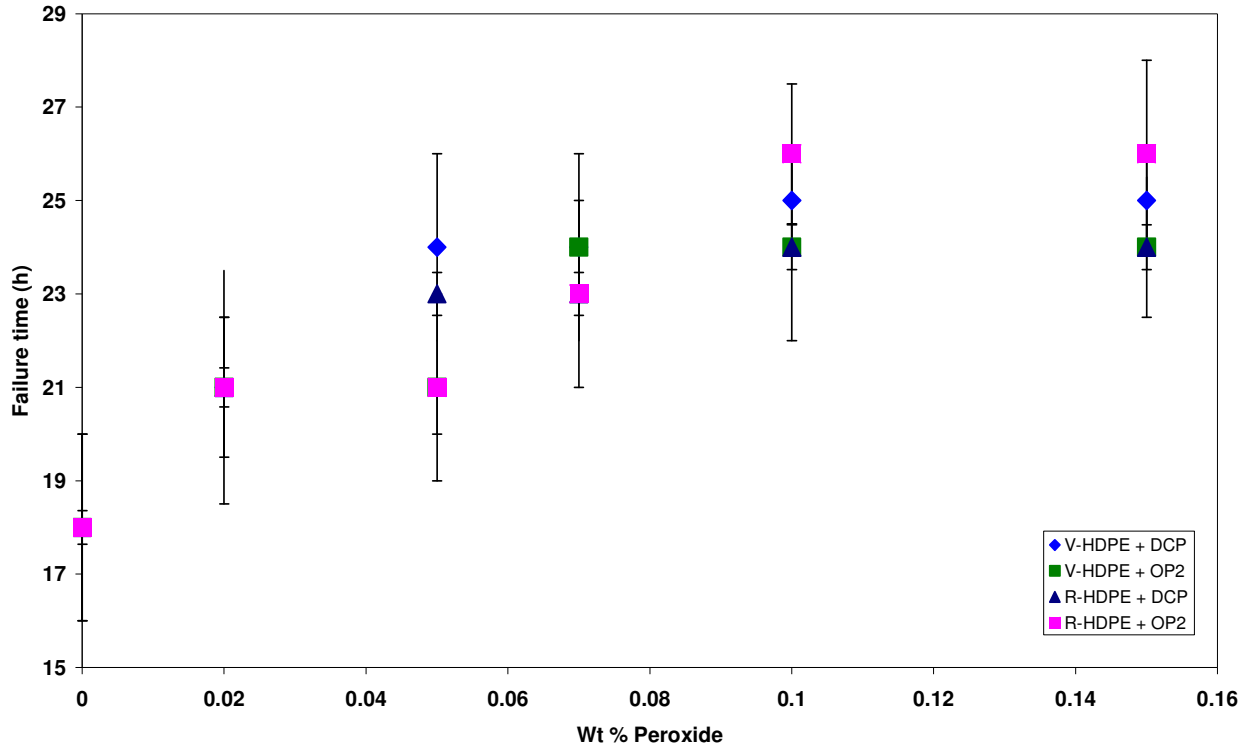


Figure 4-42 Failure time of V-HDPE and R-HDPE modified by peroxides

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

Following conclusions could be drawn from this work:

- Rheological characterisations showed that both storage and loss moduli of HDPEs increased with peroxide loading. Specifically, higher enhancements were observed at low frequency region. Moreover, decreased dependence of frequency on storage moduli at higher concentration of peroxide indicated the branched structure of the resultant material. Interestingly, OP2 peroxide modified systems showed much greater enhancement of both moduli at all frequencies compared with DCP modified systems at all frequencies. This is because of higher reactivity in terms of active oxygen content of OP2 resulting in higher degree of entanglements. Further, these entanglements reduce overall motion of the polymer and results in higher relaxation time.

- Enhancement in complex viscosity at lower frequencies and shear thinning behaviour at higher frequency were observed. Higher degree of branching revealed by modified Cole-Cole plots showed that enhancement in G' was more pronounced as compared to G" at all frequencies investigated.

- Uniaxial melt extensional measurement through Rheotens melt strength tester showed enhancement in melt strength and extensional viscosities with increase in peroxide composition for both the virgin and recycled HDPE. However, extensibility was found to decrease with peroxide concentration. These results further proved that higher degree of entanglements and less chain mobility required more force to stretch the polymer and thus increase in extensional properties.

- Thermal characterisation of the modified material showed decrease in crystallinity with enhancement of branching as peroxide loading increased for both virgin and recycled HDPE. Melting point temperature remained almost unchanged with different peroxide loadings.

- Molecular characterisation demonstrated that both molecular weights (M_w and M_n) were enhanced and molecular weight distribution (MWD) was broadened with peroxide loading. Moreover, decrease in branching index (g') proved the formation of branching mechanism in the peroxy modified materials. In addition, modified virgin and recycled HDPE polymer samples showed deviations in the Mark-Houwink plot. Moreover, higher deviations were observed with peroxide loading.

- Tensile strength of the peroxide modified HDPEs increased with peroxide loading. However, Young's modulus was found to decrease with peroxide loading since modified material is less flexible. Also small amount of filler content in the recycled material contributed to the enhancement in the Young's modulus compared to that of the corresponding virgin material. Decrease in the % elongation with peroxide loading is similar to the extensibility decrease in the uniaxial melt extensional measurement results.

- Environment stress cracking resistance increased with peroxide loading. Moreover, slow crack growth of modified material attributed to the higher degree of branching.

5.2. RECOMMENDATIONS

The following recommendations are made for possible future work:

- Change in the temperature of the drawn filament in the Rheotens melt strength tester at the initial stage of the test would be minimised by using pseudo isothermal conditions. It would be very interesting to compare the results of pseudo-isothermal condition and non isothermal condition and correction factor model could be developed for non isothermal condition.

- A pilot scale study can be carried out on modified R-HDPE materials to further test the suitability of these materials for piping applications.

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APPENDIX

SHEAR RHEOLOGY

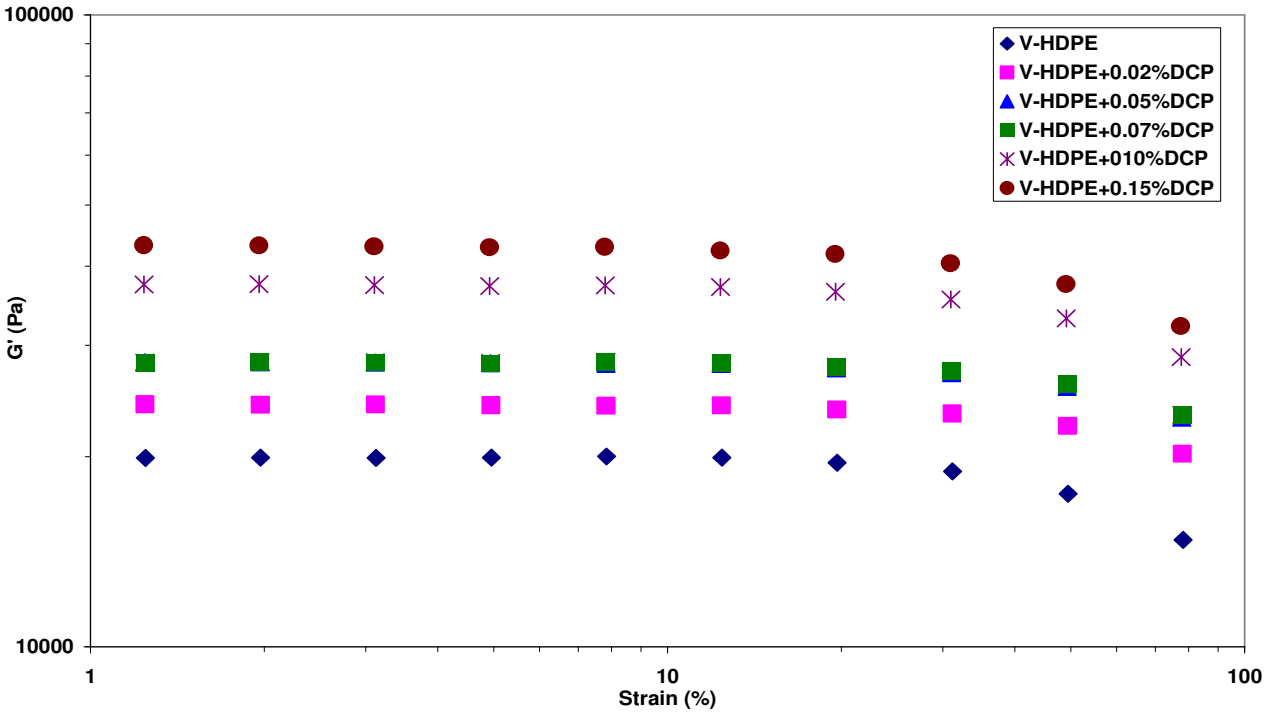

Figure A-1 Dynamic strain sweep experiments to investigate the linear viscoelastic region for V -HDPE with different compositions of DCP, at a constant frequency of 10 rad/s and 190°C

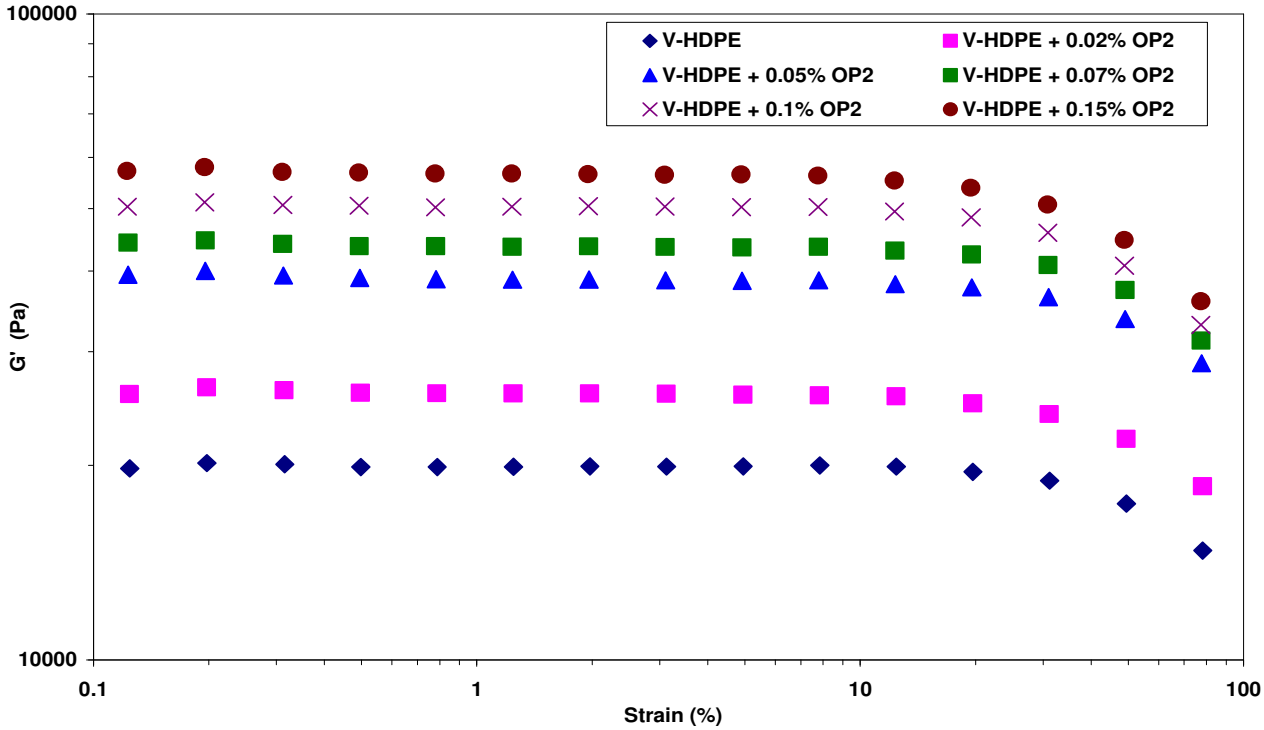

Figure A-2 Dynamic strain sweep experiments to investigate the linear viscoelastic region for V-HDPE with different compositions of OP2 at a constant frequency of 10 rad/s and 190°C

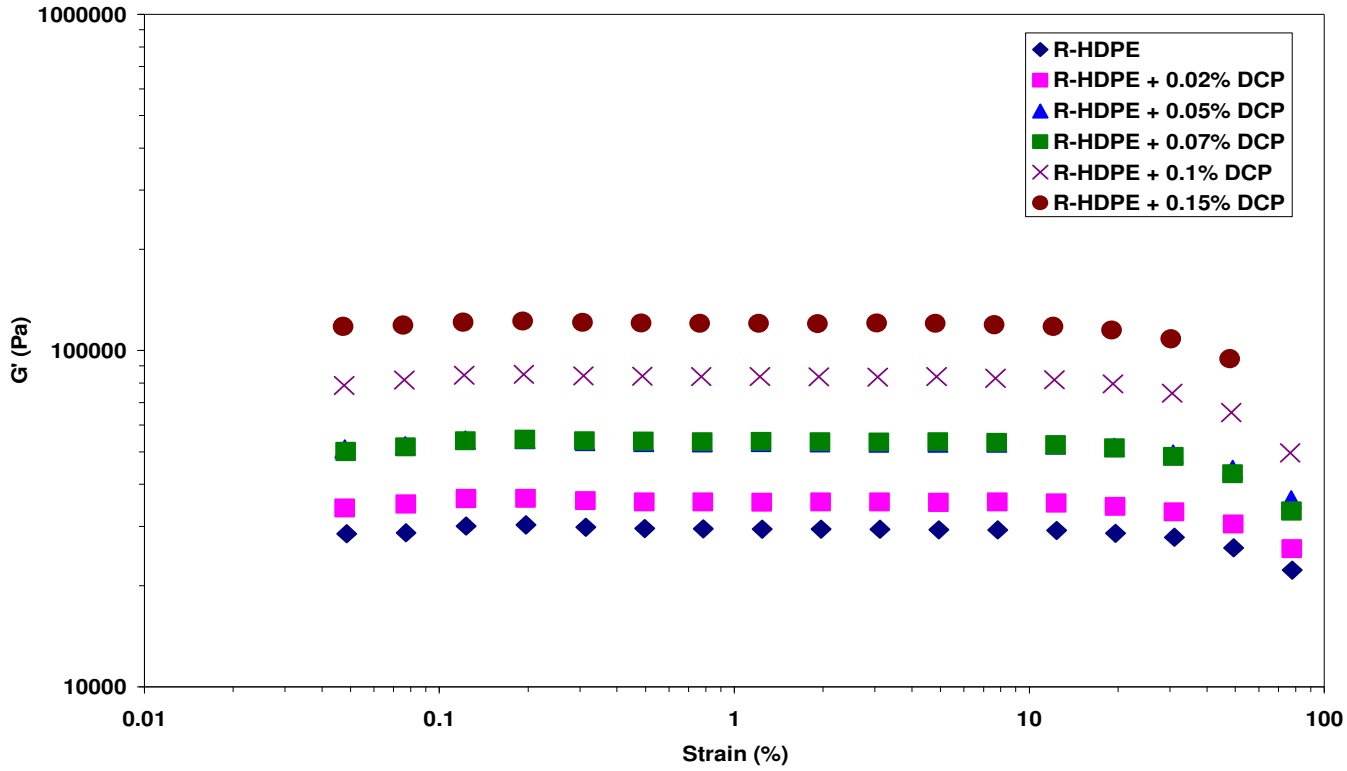

Figure A-3 Dynamic strain sweep experiments to investigate the linear viscoelastic region for R-HDPE with different compositions of DCP at a constant frequency of 10 rad/s and 190°C

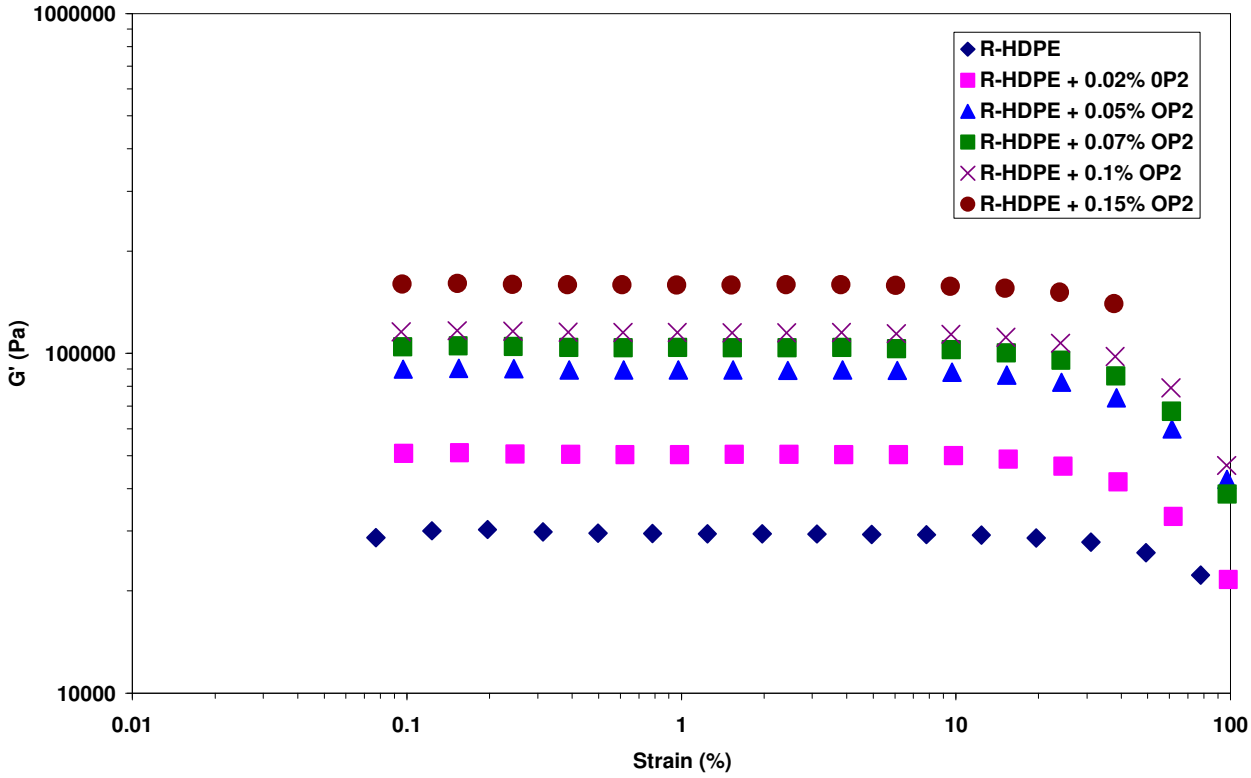

Figure A-4 Dynamic strain sweep experiments to investigate the linear viscoelastic region for R-HDPE with different compositions of OP2 at a constant frequency of 10 rad/s and 190°C

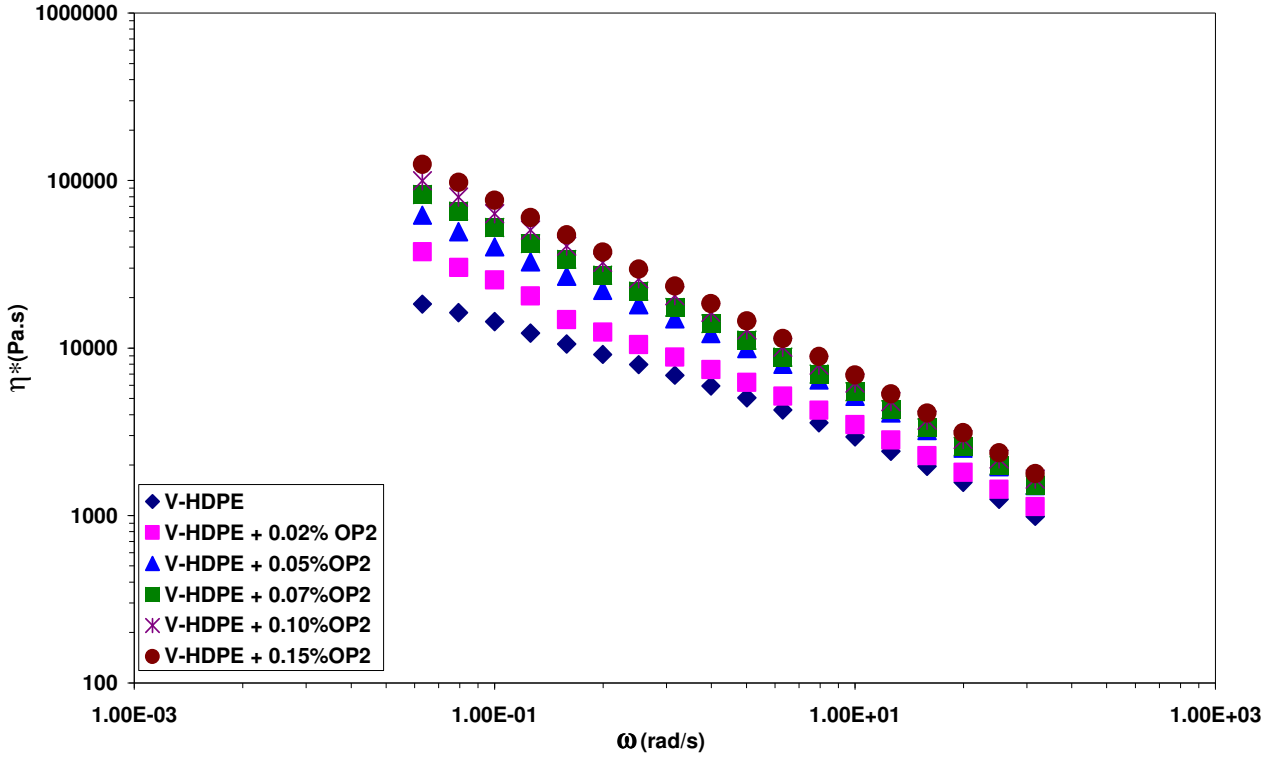

Figure A-5 Complex viscosity profile of V-HDPE + OP2 at 190 ° C

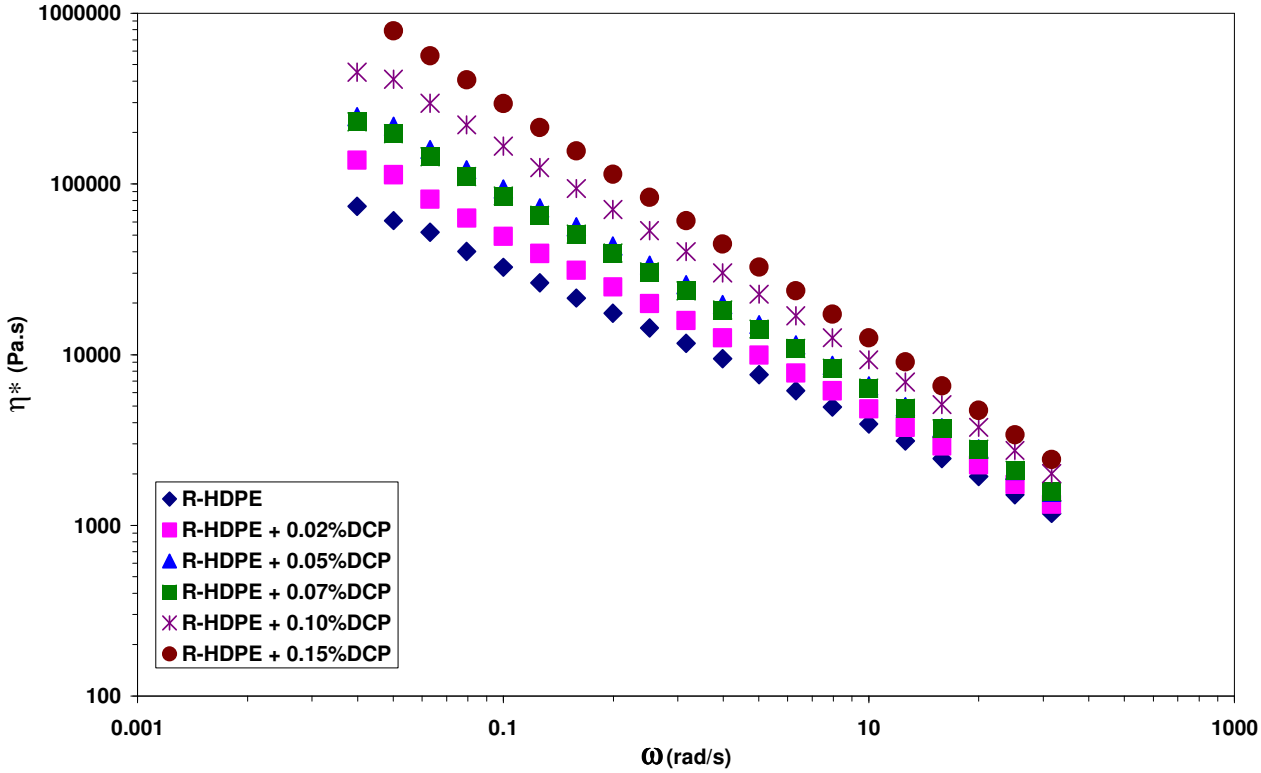

Figure A-6 Complex viscosity profile of R-HDPE + DCP at 190 ° C

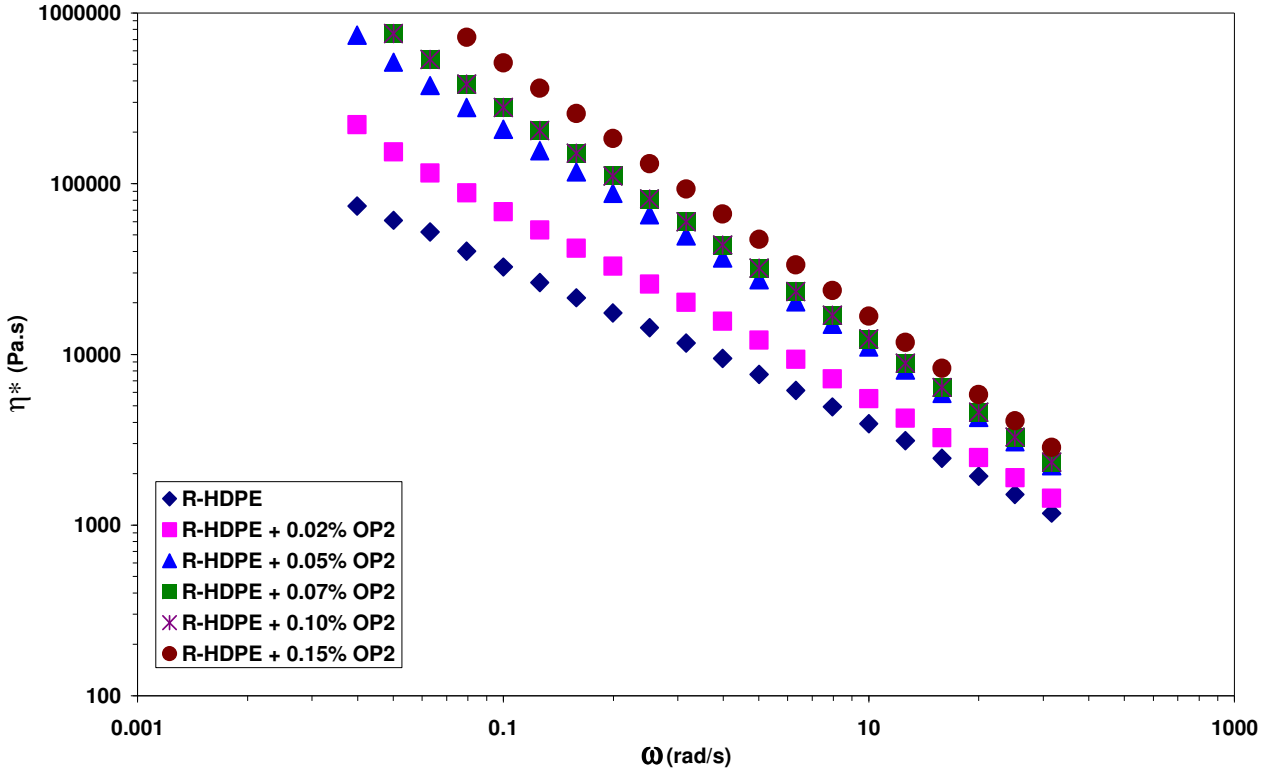

Figure A-7 Complex viscosity profile of R-HDPE +OP2 at 190 ° C

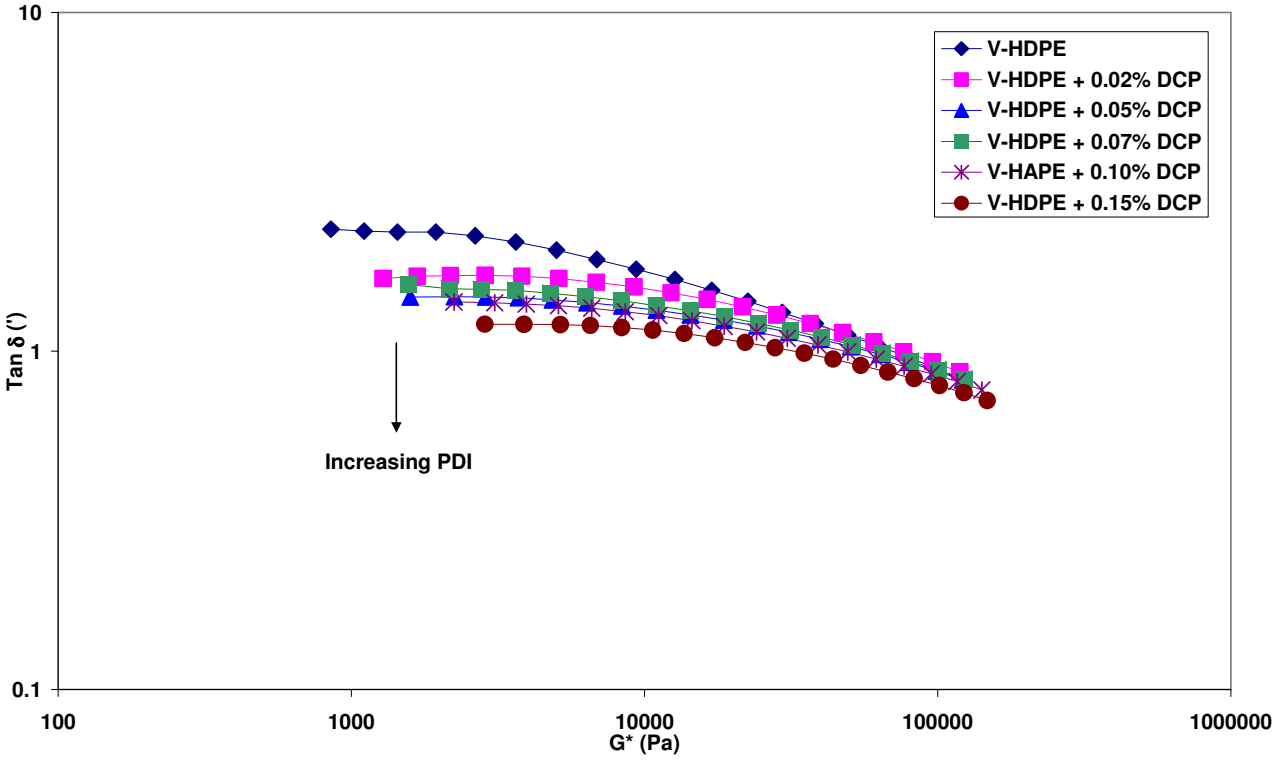

Figure A-8 Loss tangent as a function of complex modulus (tan δ – G*) for V-HDPE + DCP at 190 ° C

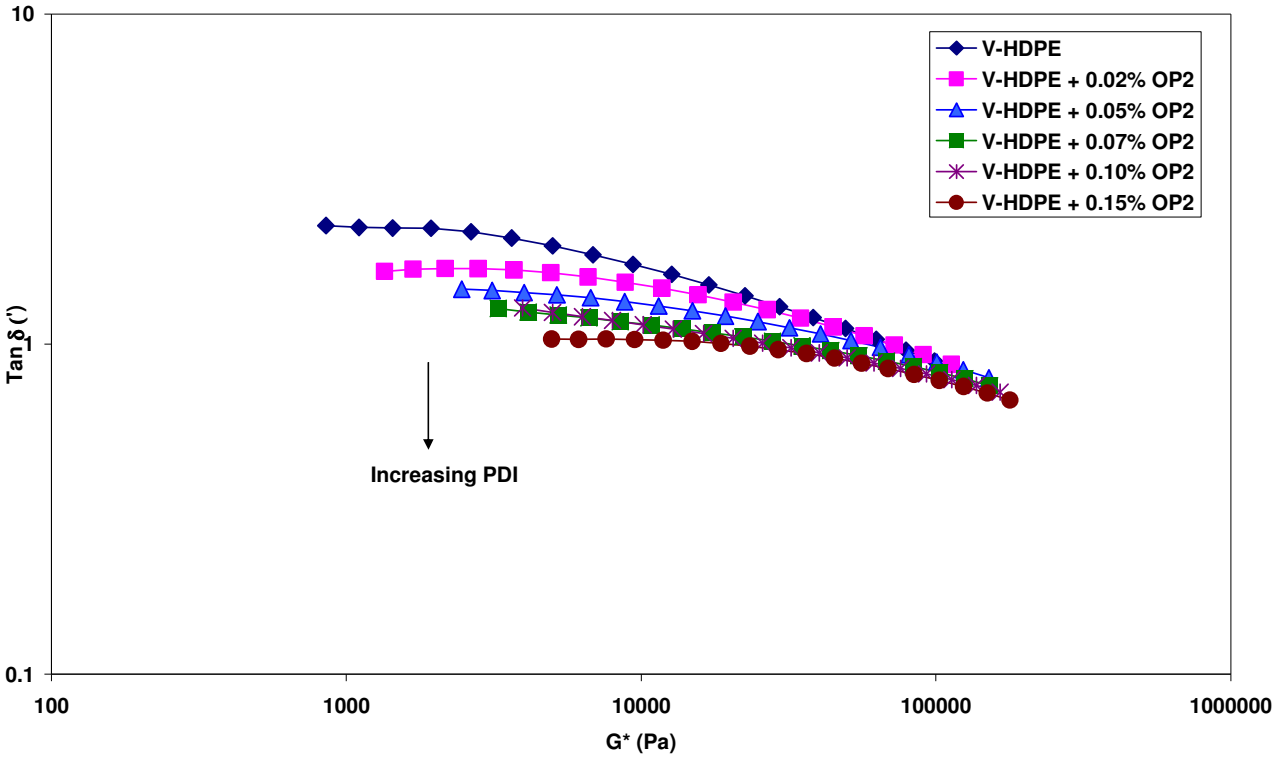

Figure A-9 Loss tangent as a function of complex modulus (tan δ – G*) for V-HDPE + OP2 at 190 ° C

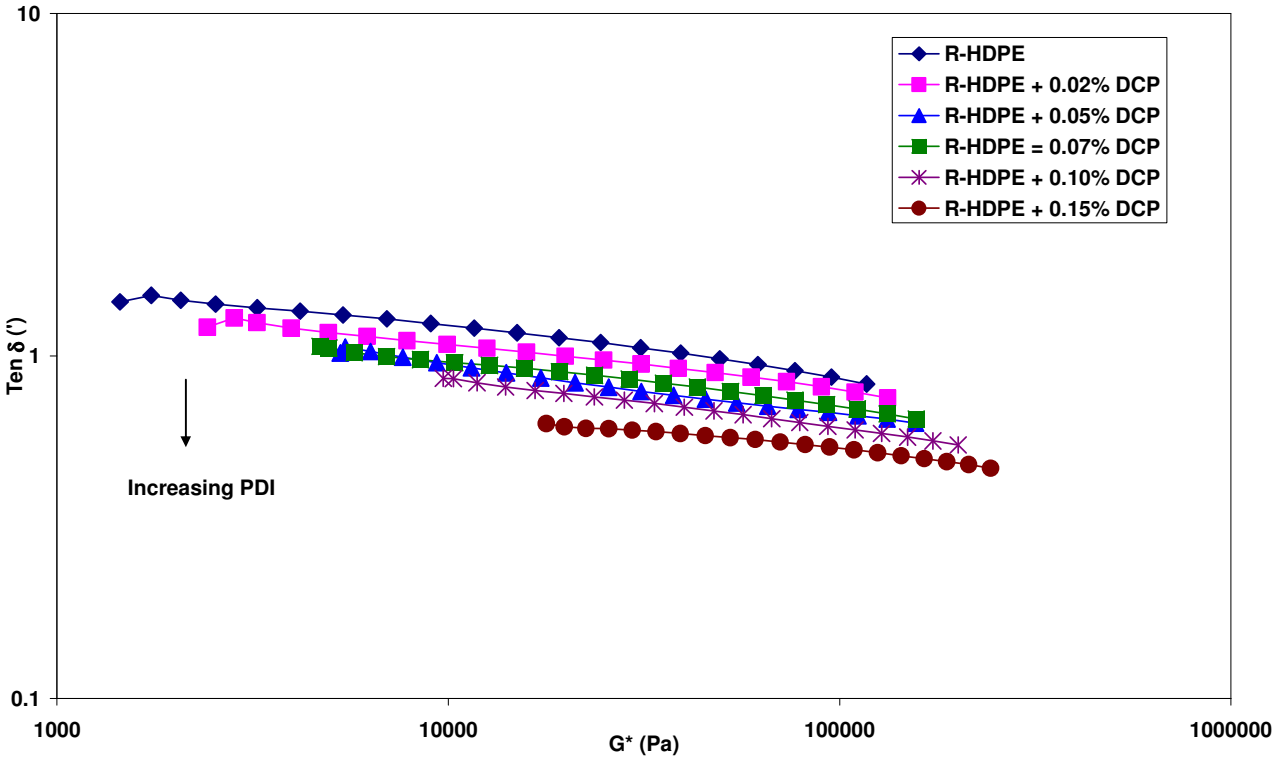

Figure A-10 Loss tangent as a function of complex modulus (tan δ – G*) for R-HDPE + DCP at 190 ° C

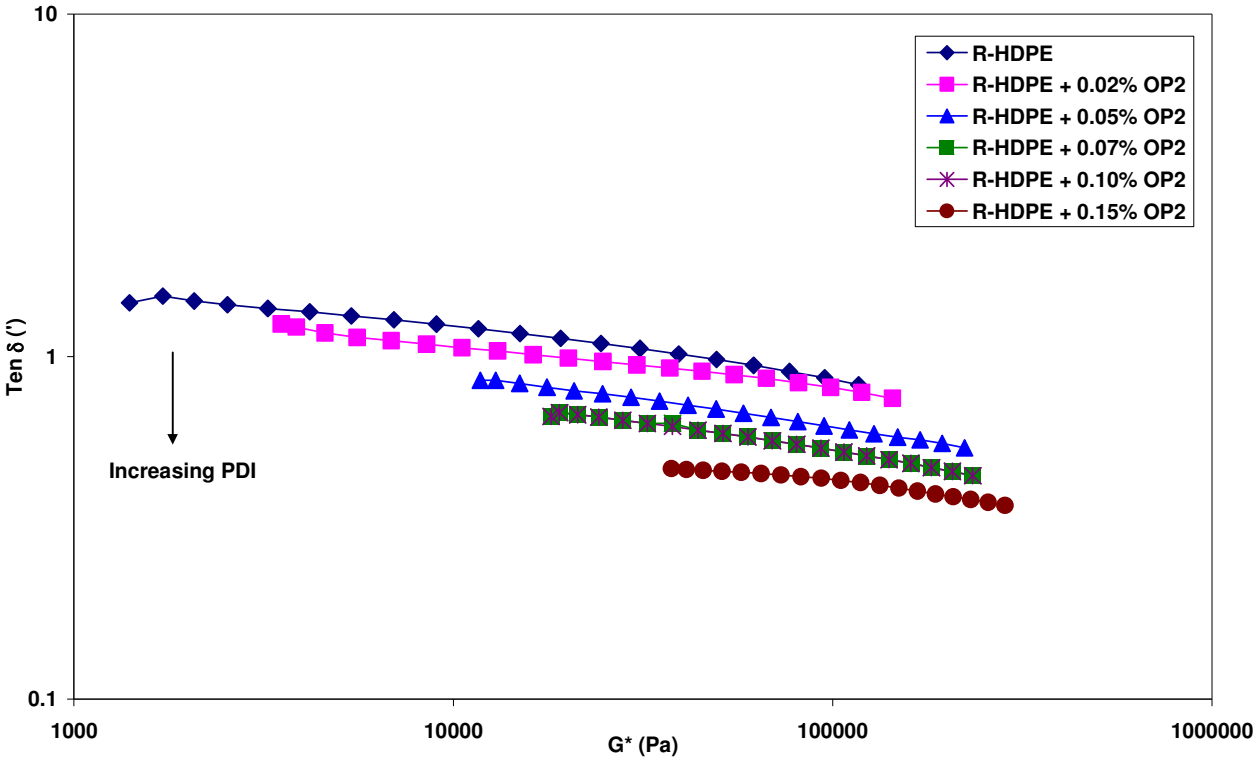

Figure A-11 Loss tangent as a function of complex modulus (tan δ – G*) for R-HDPE + OP2 at 190 ° C

GEL PERMEATION CHROMATOGRAPHY

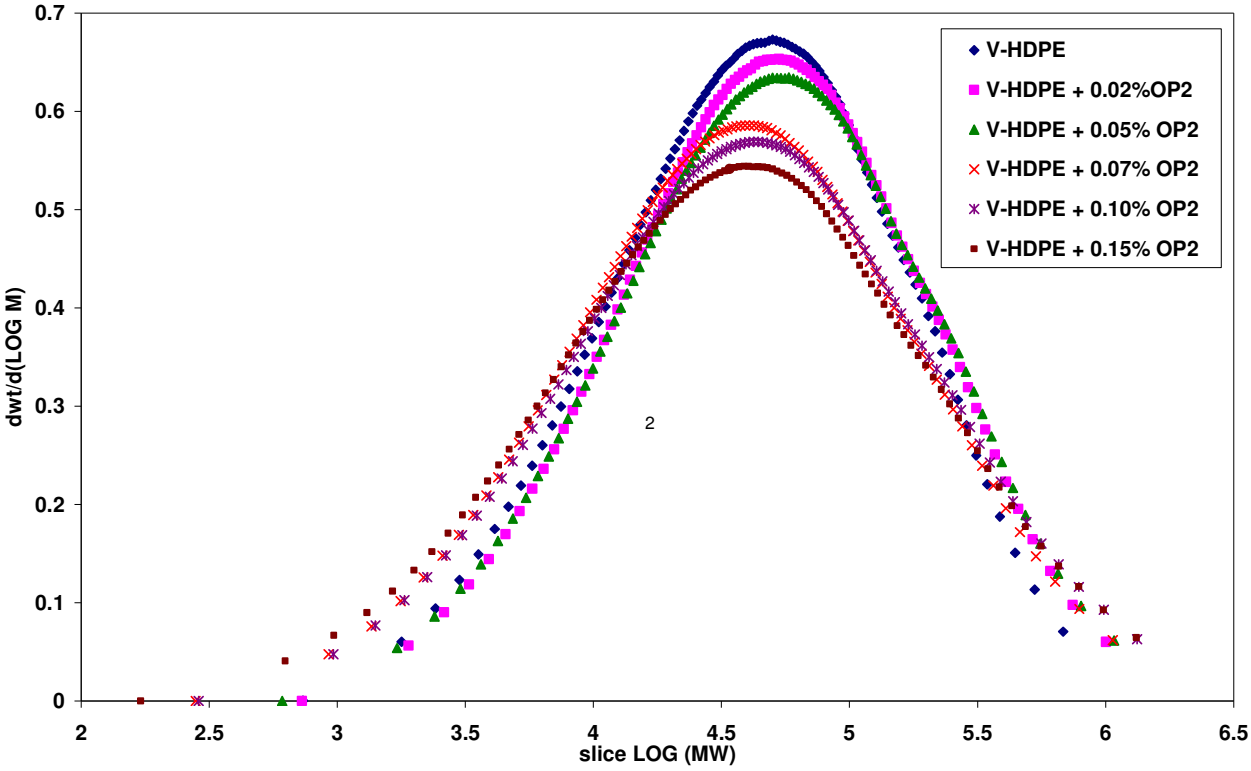

Figure A-12 Molecular weight distribution (MWD) for V-HDPE + OP2

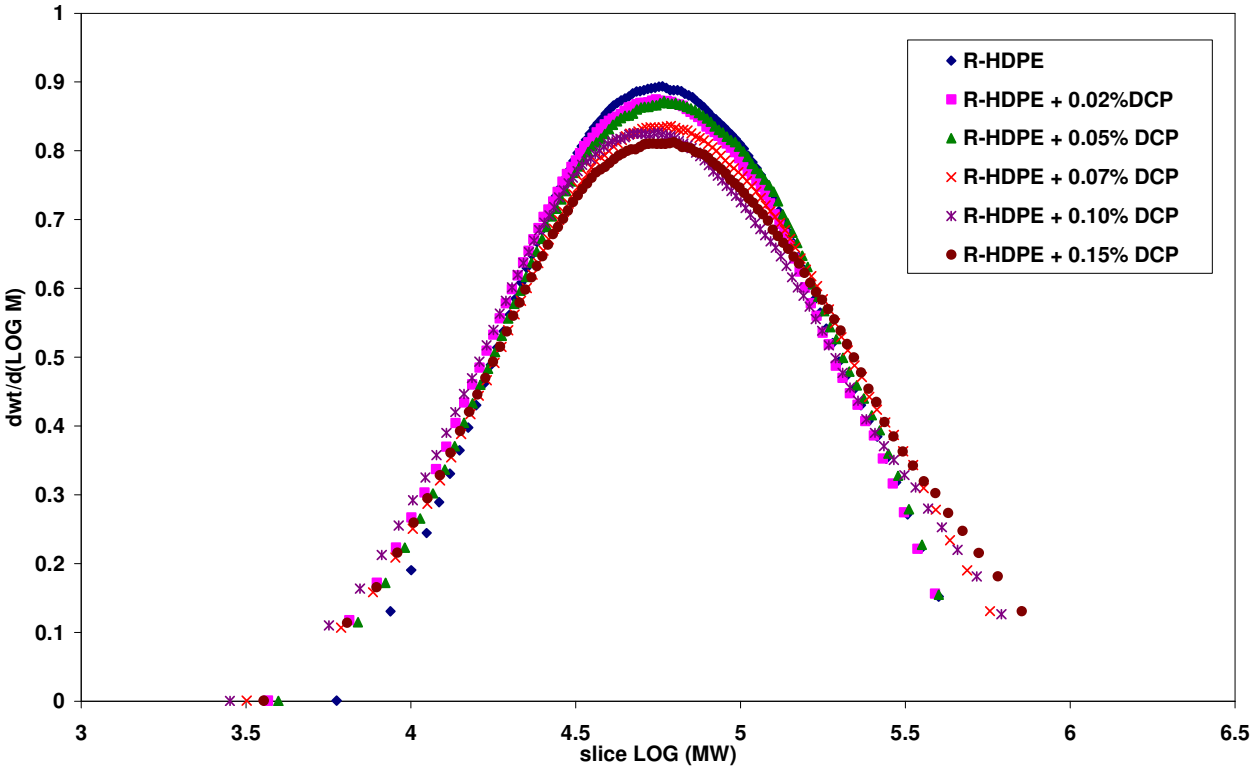

Figure A-13 Molecular weight distribution (MWD) for R-HDPE + DCP

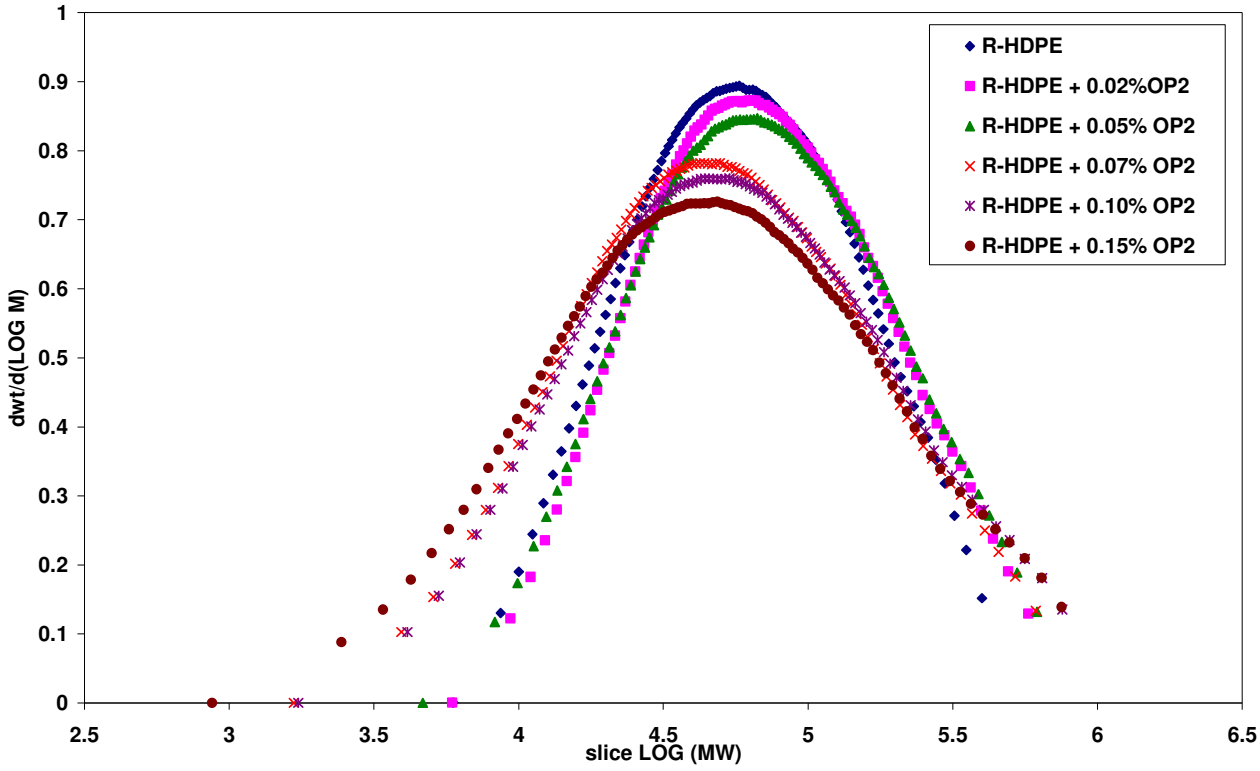

Figure A-14 Molecular weight distribution (MWD) for R-HDPE + OP2

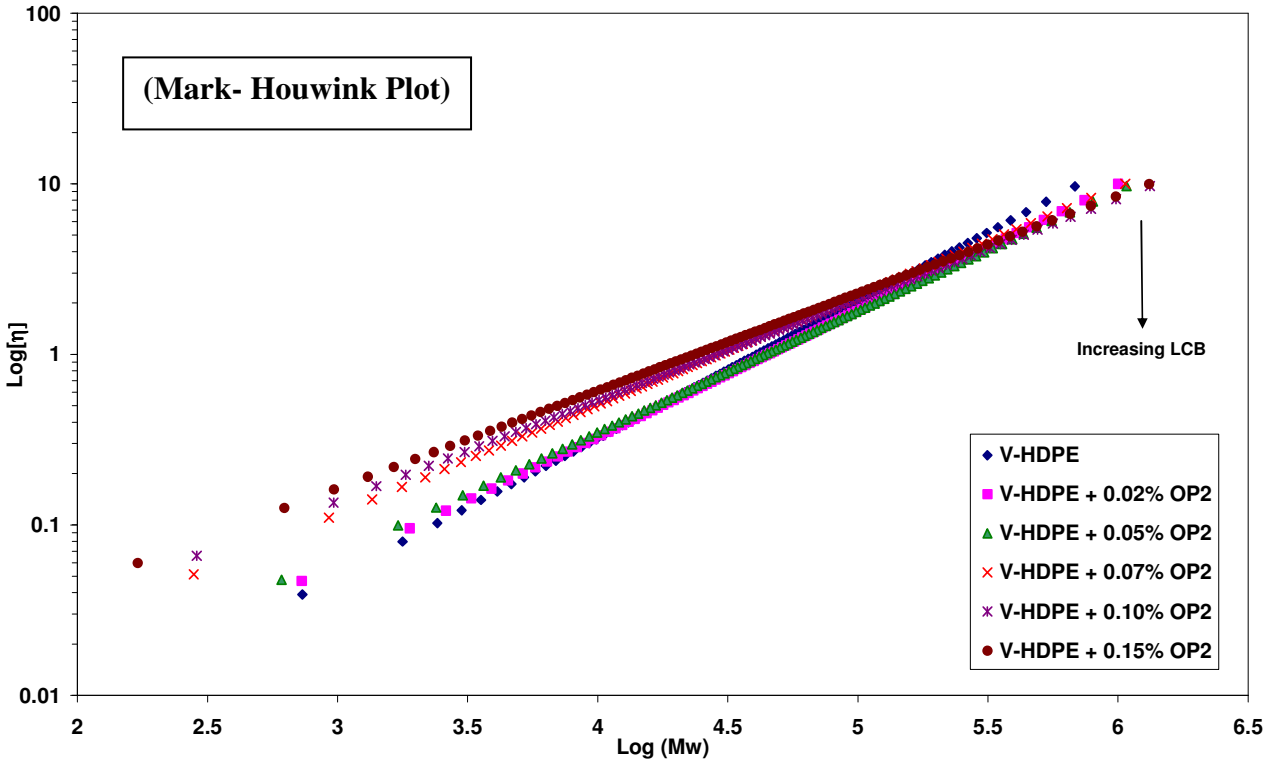

Figure A-15 Intrinsic viscosity as a function of Molecular weight for V-HDPE+OP2

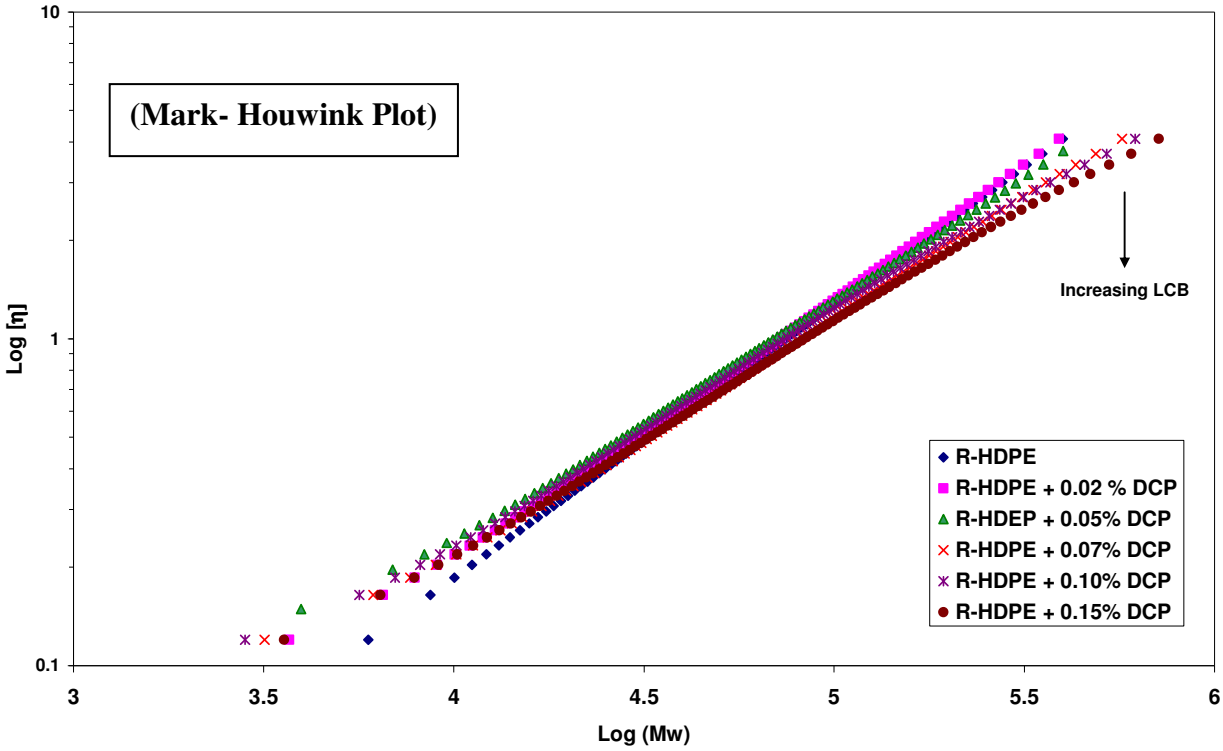

Figure A-16 Intrinsic viscosity as a function of Molecular weight for R-HDPE+DCP

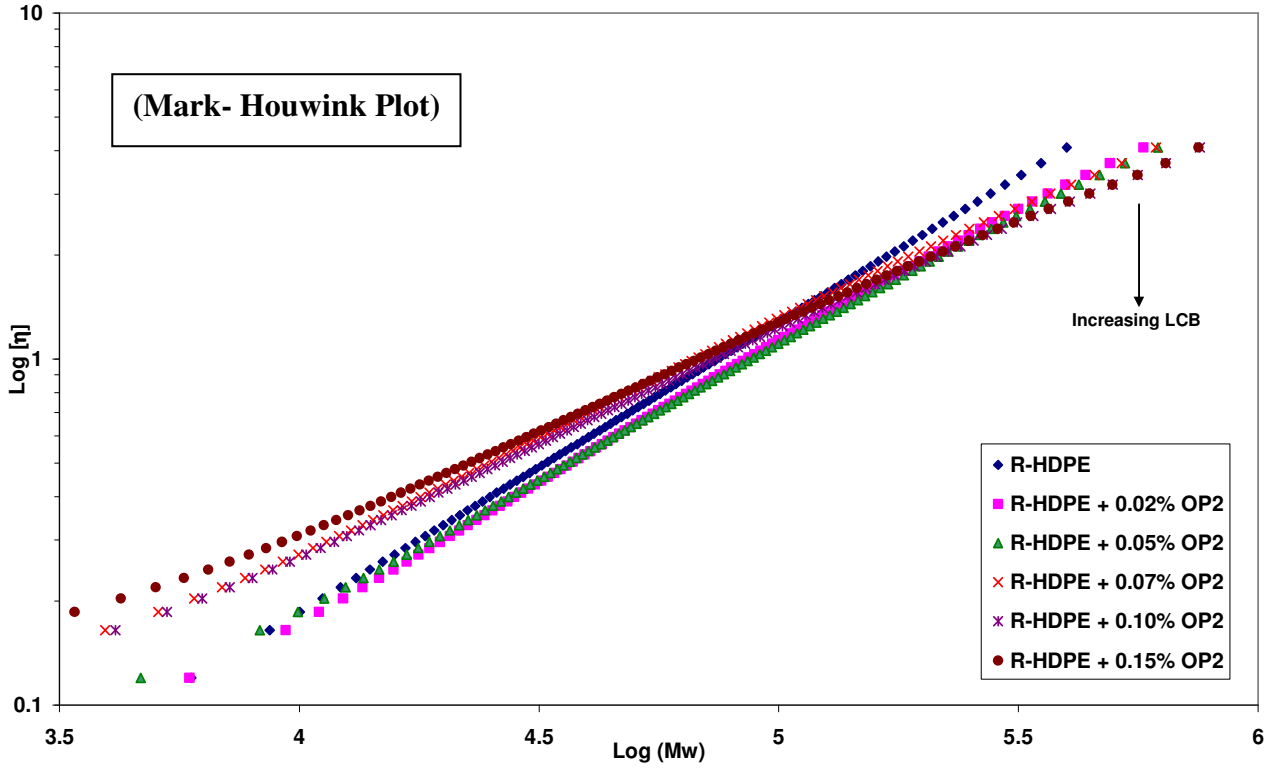

Figure A-17 Intrinsic viscosity as a function of Molecular weight R-HDPE+OP2